

Considerations in Granular Activated Carbon
Treatment of Combined Industrial Wastewaters

Texas Univ. at Dallas
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Robert S. Kerr Environmental Research Lab.
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CONSIDERATIONS IN GRANULAR ACTIVATED CARBON TREATMENT
OF COMBINED INDUSTRIAL WASTEWATERS

by

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DISCLAIMER

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities. As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (d) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

Increasing interest in the use of granular activated carbon (GAC) adsorption to improve the quality of biologically treated industrial effluents has dictated that research be performed to identify the mechanisms operating such as competitive adsorption and their potential impact on the application of GAC treatment.

Clinton W. Hall

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ABSTRACT

The effects of competitive adsorption on removal of selected organic toxicants in fixed-bed granular activated carbon adsorbers were examined using bench scale and on site adsorption systems. In bench scale studies carbon column effluents were monitored for breakthrough of substituted phenols, phthalic acid esters, chlorinated hydrocarbons, and polynuclear aromatic hydrocarbons spiked into distilled water and combined industrial wastewater matrices. A mass balance approach was used to define breakthrough curves for individual toxicants from both single and multiple solute matrices. The effect of influent concentration on adsorptive capacity was evaluated using single solute adsorption systems. High spike level single and multiple solute distilled water matrices were used to quantitatively evaluate competitive adsorption effects. Identically spiked distilled water and wastewater matrices were used to examine the effects of matrix complexity on competitive adsorption phenomena.

In all adsorption matrices investigated, polynuclear aromatics and semi-volatile chlorinated hydrocarbons were found to be the most effective competitors for available adsorption sites. More efficient removal of these compounds was found to occur not only as a result of greater carbon affinity at mutually available adsorption sites, but also as a result of adsorption at sites not accessible to the other solutes. Competitive adsorption was found to result in decreased carbon capacity for individual solutes, accelerated initial breakthrough, a more rapid breakthrough rate, and desorption of lower affinity compounds. Results from site studies on adsorption of common toxicants from unspiked wastewaters revealed adsorption patterns supportive of bench scale studies. The site study data indicate that in competitive adsorption environments, the relative concentration levels of individual species will have a pronounced effect on their ability to compete for available adsorption sites.

Effluents from carbon columns treating low spike level wastewater matrices were also monitored for breakthrough of surrogate organic parameters, including TOC, COD-digestion, and COD-UV correlation. These data were examined to determine how accurately breakthrough of the surrogate column monitoring parameters reflected the breakthrough of specific organic toxicants. Surrogate parameter breakthrough curves were found to be radically different from those exhibited by individual toxicants, severely limiting effective use of such parameters as carbon column monitoring tools. None of the three surrogate monitoring parameters proved to be sensitive detectors of low affinity toxicant breakthrough, indicating that more specific techniques will be required to efficiently monitor carbon column effluents.

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INTRODUCTION

Granular activated carbon (GAC) column treatment has been suggested as an alternative for removal of low level synthetic organic compounds (SOC) that have survived conventional treatment processes applied to industrial wastewaters. Numerous studies, both laboratory scale and pilot plant, have shown GAC to be effective in removing trace organics from aqueous systems. However, much of this research has concentrated on relatively clean water systems. Removal of low concentrations of SOC from a complex wastewater presents certain problems that have yet to be satisfactorily addressed in the literature. This study was designed to examine some of these problems.

The phenomenon of competitive adsorption is the primary focus of this research effort. Different organic compounds show different affinities for the activated carbon surface. These differences are manifested in such determinations as isotherm studies and carbon column capacity evaluations and are primarily related to such factors as hydrophobicity, molecular configuration and polarity. Weber and Morris (1964) and subsequently others have described suppression of adsorption of one compound by the presence of a second compound in the aqueous system. Logically, the compound showing higher carbon affinity should effectively outcompete the other compound for the adsorption sites; hence the observed suppression.

Advanced wastewater treatment of industrial wastewaters seeks to remove or reduce concentrations of specific "toxic" pollutants in the effluent stream. The competitive adsorption phenomenon could influence the ability of a GAC system to accomplish this goal. The presence of a variety of toxic pollutants in the wastewater could result in the retention of certain of these toxics on the GAC at the expense of other equally toxic compounds. In addition, the natural products of the treatment process (represented as effluent total organic carbon) could influence the adsorption of those compounds of concern. Thus, an added burden of monitoring for the most mobile of those compounds is placed on the system operator, and the economic feasibility of using GAC in this application becomes less clearly defined.

A combined industrial wastewater effluent, treated in a conventional extended aeration system, was selected as the study matrix. Twelve SOC identified by the U.S. Environmental Protection Agency (USEPA) as being present in the effluent were selected for evaluation in this study. The nature and extent of the competitive adsorption phenomenon was examined in

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a series of bench-scale column adsorption studies using both pure and waste-water matrices. These studies defined patterns of competitive adsorption for the organic compounds investigated. The applicability of these data was then evaluated using onsite treatment of the combined wastewater effluent through scaled-up pilot GAC columns. The suitability of using conventional column monitoring techniques, specifically total organic carbon (TOC) and chemical oxygen demand (COD), when removal of specific pollutants is of primary concern was also evaluated.

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CONCLUSIONS

This study has shown that adsorption of specific organic toxicants in fixed-bed granular activated carbon adsorbers is a complex phenomenon even in relatively simple water matrices. On a relative basis, carbon affinities of the toxicants studied were fairly consistent in all matrices investigated, decreasing according to the following general trend: PNA's = semi-volatile chlorinated hydrocarbons > phthalate esters = disubstituted phenols > monosubstituted phenols = 1,1,2,2-tetrachloroethane > phenol. In multiple solute adsorption systems, competitive adsorption interactions resulted in varying degrees of reduction in removal efficiency for individual solutes. The presence of high carbon affinity constituents resulted in substantial suppression of adsorptive capacity for lower affinity species in the competitive adsorption environments, but the presence of lower affinity compounds exerted little influence on removal of higher affinity ones. In addition to suppression of adsorptive capacity, competitive adsorption interactions resulted in accelerated initial breakthrough, a more rapid breakthrough rate, and desorption of lower affinity compounds. The data indicate that the reduction in removal of lower affinity compounds occurred as the result of at least two distinguishable phenomena, including: 1) less effective competition at mutually available adsorption sites; and, 2) displacement of previously adsorbed lower affinity species.

In addition to adsorbate type, the magnitude of influence exerted by competitive adsorption interactions was highly dependent upon water matrix composition. Competition from background wastewater constituents, obscure at higher spike levels, became extensive in lower spike level matrices. In these matrices, background constituents were able to successfully compete for adsorption sites even though relative concentration levels likely afforded spike components a competitive advantage. The effects of relative concentration levels were even more pronounced in the unspiked wastewater matrix used in site studies. In this matrix, where study toxicants were present at substantially lower concentration (relative to background constituents) competitive adsorption interactions resulted in greatly accelerated initial toxicant breakthrough. The influence of matrix composition and relative concentration levels on competitive adsorption phenomena will undoubtedly require that on site adsorption studies be conducted on the specific wastewater to be treated to optimize carbon performance, accurately assess treatment feasibility, and determine

monitoring strategy. For the secondarily treated industrial wastewater used in this study, GAC was shown to be a technologically feasible technique for controlling organic toxicants. GAC treatment was initially capable of reducing effluent toxicant concentrations to below detection levels, even when spiked at relatively high concentration levels. However, in the absence of criteria concerning acceptable effluent toxicant levels or ambient water quality, economic feasibility is difficult to assess.

The complexity of competitive adsorption interactions also limits the use of simple parameters such as adsorbate characteristics or batch adsorption data for prediction of carbon performance, and complicates effective column monitoring. In simple single solute systems, batch data and aqueous solubility proved to be useful indicators of relative carbon affinity, although no simple correlation was found with n-octanol/water partition coefficients for the compounds tested. However even in single solute matrices, lack of information concerning the shape of the breakthrough curve remains a limitation in the use of such parameters for predicting carbon performance in continuous-flow applications. These parameters provided no information regarding initial adsorbate breakthrough or the rate of breakthrough upon subsequent column operation, characteristics of great importance in wastewater treatment applications.

The complexity of competitive adsorption phenomena currently preclude accurate prediction of carbon column performance in wastewater matrices. As a result, effective use of GAC as a pollution control technology is dependent upon sensitive, accurate column monitoring. Results from this study clearly indicate that effective column monitoring must be based upon detection of the most mobile toxicant within the matrix to be treated. The data indicate that monitoring with the use of surrogate parameters such as TOC or COD will be complicated by their radically different breakthrough characteristics, relative to those exhibited by individual toxicants. Surrogate parameter breakthrough curves were characterized by very rapid initial breakthrough, followed by a prolonged, fluctuating ascent to approximately 80% breakthrough. This breakthrough pattern resulted in: 1) poor sensitivity for detection of individual toxicant breakthrough; and, 2) poorly defined breakthrough points, making the use of a percentage breakthrough monitoring approach tenuous, at best. TOC and COD measurements provided insufficient indication of even gross changes in toxicant effluent levels such as desorption. Sensitivity with this approach would undoubtedly become an even greater problem at lower toxicant concentration levels. The data suggest that efficient detection of toxicant breakthrough will necessitate the use of more specific monitoring techniques to achieve the sensitivity required for effective column monitoring.

It is likely that some of the competitive adsorption phenomena observed in this study are affected by the types and concentrations of solutes chosen for spiking into the test matrices. It is also conceivable that the choice of columns and carbon size may have influenced the results. However, replicate column runs proved quite reproducible and bench-scale data was generally supported by field study-investigations, indicating it is likely that the adsorption patterns observed are representative of competitive adsorption interactions occurring in complex wastewater matrices.

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RECOMMENDATIONS

If removal of toxic organic pollutants to levels below those obtainable by conventional treatment processes is required, then granular activated carbon treatment should be considered as one alternative. However before such treatment is mandated, it is recommended that several issues be addressed. Initially, acceptable risk levels for the pollutants of concern must be established in terms of effluent guidelines, or ambient water quality criteria, before a meaningful evaluation of feasibility can be undertaken. Once established, on-site adsorption studies should be initiated to assess both technological and economic feasibility of attaining such criteria on a case by case basis. Finally, research efforts are needed to explore alternate column monitoring techniques. It is clear that effective carbon column monitoring will have to either: 1) identify and follow the breakthrough of the most mobile component of concern; or, 2) establish the relationships between breakthrough of any surrogate parameter employed and the most mobile component of concern. Even if a surrogate parameter of adequate sensitivity/specificity is employed, effective use of such a parameter will likely require an extremely consistent column influent composition.

Based on this study, it is also recommended that research efforts should continue to be focused on developing a better understanding of competitive adsorption phenomena. The role of relative concentration level is a particularly important (and poorly understood) factor in competitive adsorption interactions. The influence of concentration in competitive adsorption environments is of obvious significance in practical applications, and efforts should be centered on exploration of this phenomenon from both qualitative and quantitative aspects.

Two other issues also merit further investigation. As assessment of how representative the competitive adsorption patterns observed for the toxicants used in this study are of those occurring for organic toxicants in general would be of great value. If these patterns are representative of other organics, or of related species, then useful generalizations could perhaps be employed. Along these lines, the relationships between adsorption phenomena and adsorbate characteristics deserves further exploration. A standardized methodology should be developed for aqueous solubility and n-octanol/water partition coefficients for hydrophobic compounds to more accurately evaluate their utility as indicators of adsorbate affinity in competitive adsorption environments.

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LITERATURE REVIEW

CHEMISTRY OF ACTIVE CARBON SYSTEMS

The adsorption of organic solute molecules from aqueous solution is a complex phenomena involving the interaction of chemical and physical forces. The adsorption phenomena can be generally described as the concentration of molecules at a surface or interface, and occurs as a result of forces active within surface boundaries. Various forces having their origin in the electromagnetic interactions of nuclei and electrons exist between molecules in proximity to a solid surface and the surface molecules. Two types of binding forces, physical; and chemical, are commonly distinguished between a surface and foreign molecules. Physical adsorption, which predominates in active carbon systems, results from the action of van der Waals forces, comprised of London dispersion forces and classical electrostatic forces. In this context, the electron distributions of adsorbate molecules and solid surface molecules undergo some distortion in mutual proximity; however, the electrons maintain their association with the original nuclei (Weber, 1974). According to the quantum mechanical perturbation theory developed by London (1930) the continuous motion of electrons in atoms and molecules effect rapidly fluctuating temporary dipole and quadrupole moments. Such fluctuating dipole and quadrupole moments in foreign molecules approaching a solid surface can perturb the electron distribution of surface molecules to induce temporary dipoles and quadrupoles therein. These induced dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole attractive interactions constitute the London dispersion forces of physical adsorption. These attractive potentials are nonspecific and operate between polar and nonpolar molecules, but act only over very short distances.

The other component of van der Waals forces, classical electrostatic interactions (Clark, 1970) are more specific than dispersion interactions and are especially prevalent between polar molecules and ionic or heteropolar solids. Attraction potentials are generated by the polarization of the molecules within the electric field of the solid surface. These potentials are dependent upon the surface electric field strength and the polarizability of the adsorbate molecules.

The second important category of adsorbate-solid surface interaction is termed chemisorption, an adsorptive mechanism much more specific than physical adsorption. As a result of significant solute-surface

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affinities, molecular orbital overlap occurs between molecules in the respective phases. Transfer and/or sharing of electrons take place between adsorbed solute and adsorbent, and the chemisorptive bond has all the characteristics of a chemical bond. The chemisorptive bond is localized at active centers on the adsorbent and is generally stronger than the physical van der Waals forces, resulting in enhanced adsorption for adsorbates capable of this type of bonding.

Adsorption from solution occurs in four steps: 1) the organic molecules migrate through the bulk solution to the carbon particle; 2) a solute molecule is transported across a surface film to the exterior carbon surface; 3) it then diffuses into the pore structure; and 4) it is finally adsorbed onto a specific site on the internal surface. The adsorption mechanism is strongly influenced by factors associated with the adsorbent, the adsorbate, and the complexity of the aqueous system. Although it becomes difficult to distinguish the effect of individual factors, each likely contributes significantly to the intensity of sorbate-sorbent affinity.

Factors Associated With The Adsorbent

The efficiency of an adsorbent for removing organics from water depends upon its component raw materials and the process by which it was manufactured. Raw material, the activation process, and post activation conditions determine final adsorbent characteristics, which in turn influence the adsorptive mechanism. Currently, all activated carbons are produced by one of two processes: chemical activation or physical activation, using high temperature controlled oxidation. In either case, the process primarily consists of two steps; initially a carbonaceous material is charred, and then the char is selectively oxidized to create an internal pore structure (Dubinin, 1966). During char production, the source material is heated in the absence of air to a temperature sufficient to effect drying and to drive off volatile fractions. In this process the temperature is increased slowly to allow time for each step to be completed before the next begins, and final temperatures are held below 600° C (Hassler, 1963). The char is subsequently activated by treatment with oxidizing gases under carefully controlled conditions. The oxidizing gases, commonly carbon dioxide, steam, and air, attack the more readily oxidizable portions of the char, resulting in the development of a porous structure with an extensive internal surface (Johnson et al., 1964). The temperature of activation is the most critical factor in the process, and may range from 400-1000° C. Pores that are less than 100Å are termed micropores, pores between 100Å and 1000Å transition pores, and those greater than 1000Å are macropores.

Coconut shells, peat, pecan shells, pulp mill black ash, wood, petroleum base residues, lignite, and bituminous coal are source materials which have been used in the production of active carbons (Donnet, 1968). However, for broad spectrum applications commonly encountered in wastewater treatment, lignite and bituminous coal are the active carbon precursors of choice. A comparison of adsorbent characteristics typically associated with active carbons prepared from lignite and bituminous coal

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is presented in Table 1.

Adsorbent characteristics most influential in determining adsorption efficiency and adsorbate affinity include surface area, pore structure, chemisorbed oxygen, surface polarity, and particle size. Because adsorption is essentially a surface phenomena, surface area and pore structure are the most important characteristics in determining adsorption capacity. Since pore structure and surface area are defined by the activation process and source material, careful control of these parameters is essential.

On a mass adsorbed per unit mass of carbon basis, increasing carbon surface area results in greater carbon capacity. Although the total surface area of an active carbon can be as great as 2,500 m²/gram after activation, this relationship is true only to a level of about 1,500 m²/gram of carbon (Johnson, 1964). At and above this level, increased surface area is produced by means of so fine a pore size (less than 1 nm diameter) that only the smallest organic molecules can be accommodated. The micropores in active carbons are developed by burning away a complete layer of the fused carbon rings within the microcrystalline carbon structure (Snoeyink and Weber, 1967). Adsorption sites for activated carbons are located at the walls of the micropores, and at the pure carbon surface (Glushchenko et al., 1975).

Pore structure can influence both adsorptive capacity and adsorption rate, which is the rate of mass transfer of adsorbate molecules from the bulk solution to specific adsorption sites. Pore structure influences adsorptive capacity through the relationship between adsorbate size and pore size. If the majority of the pore structure consists of small micropores (less than 1 nm in diameter), larger organic molecules are excluded from the pore system by size alone. The greatest percentage of available surface area of active carbons exists within the micropore structure, so when adsorption can only occur on the pure carbon surface, capacity is greatly reduced.

Pore structures influence the rate of mass transfer because in most cases of adsorption from aqueous solution, diffusion through the pore structure is the rate limiting step (Zanitsch and Stenzel, 1978). Migration of adsorbate molecules to the carbon surface and transfer across the surface film occur rapidly relative to transport within the internal pore structure to final adsorption sites. Before more adsorbate molecules can be removed from solution, molecules currently residing at the carbon surface must be transported internally. Therefore, those organic molecules that barely fit inside the pores diffuse very slowly into the interior of the carbon particle and limit the rate of removal of other sorbate molecules in solution. In heterogeneous systems, such as wastewater matrices, adsorptive efficiencies are maximized by utilizing carbons in which the pore structure has a balanced distribution of micropores, transition pores, and macropores.

Directly related to surface area phenomena is the influence of carbon particle size. As the size of the carbon particle is reduced, the total available surface area per unit mass of adsorbent is greatly increased. This increase is a result of increase in pure surface area by having more spheres per unit mass, and also by having more available pore area. A larger carbon particle will have a greater extent of internal pore structure, but because of pore constriction and blockage, a considerable

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TABLE 1. COAL SOURCE ACTIVE CARBON CHARACTERISTICS⁽¹⁾

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	8 x 30 Mesh		12 x 40 Mesh	
	Bituminous Coal Carbons	Lignite Carbons	Bituminous Coal Carbons	Lignite Carbons
Total Surface Area, m ² /g	950-1050	600-650	1000-1200	650-700
Iodine No., minutes	950	600	1050	650
Bulk Density, g/cm ³ (Backwashed and Drained)	0.42	0.35	0.42	0.35
Particle Density Wetted in Water, g/cm ³	1.3-1.4	1.3-1.4	1.3-1.4	1.3-1.4
Pore Volume, cm ³ /g	0.85	1.0	0.94	1.0
Effective size, mm	0.80-0.90	0.75-0.90	0.55-0.65	0.55-0.65
Uniformity Coefficient	≤1.9	≤1.9	≤1.9	≤1.9
Mean Particle Diameter, mm	1.6	1.5	1.0	0.85
Pittsburg Abrasion No.	70-80	50-60	70-80	50-60
NBS Abrasion No., % Retention/mm	70-75	74-82	70-75	74-82
Moisture as Packed, Max.	2%	9%	2%	9%
Molasses Relative Efficiency	40-60	100-120	200-300	450-500
Ash	5-8%	12-18%	5-8%	12-18%
Mean Pore Radius	14 Å	33 Å	14 Å	31 Å

(1) Modified From DeJohn (1974).

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portion of the total length may rapidly become unavailable for adsorption. Therefore, although individual particles have less pore length, the amount of available pore area is substantially greater for smaller mesh particles, because pore paths are shorter so constriction becomes less significant.

The influence of carbon particle size on the adsorptive mechanism has been studied by numerous investigators. Zogorski and Faust (1976) studied the effect of particle size on the breakthrough characteristics of several phenolic adsorbates in continuous flow systems. They found that decreasing the size of the adsorbent increased the time until initial column breakthrough for carbons down to 25 x 30 mesh (0.7 mm), but initial breakthrough was independent of the size of the adsorbent for particle sizes less than 25 x 30 mesh. They concluded that the steepness of the breakthrough curve was dependent upon particle size, but that the rate of movement of the mass transfer zone (adsorbate front) was independent of particle size. The independence of movement implies that adsorptive capacity is also independent of particle size. This observation is in agreement with earlier studies by Zogorski and Faust (1974), under non-flow equilibrium conditions, and also with those of Weber and Keinath (1967). Despite differing viewpoints on this topic, there appears to be insufficient evidence to prove that carbon capacity is related to particle size for organic compounds of moderate size. This is particularly true for continuous-flow systems in which short residence times prevent adsorptive equilibria from being reached.

Surface polarity and chemisorbed oxygen play a major role in determining adsorbent efficiency and selectivity. Evaluations of the adsorptive behavior of active carbons based solely on surface area considerations are incomplete, for carbons of equal surface area but differing surface activity exhibit significantly different characteristics. Part of such differences in behavior can be explained in terms of relative pore size distributions, but part must also be attributed to differences in surface properties of the carbons. The surface of any active carbon is comprised in part of ion-exchange functional groups, connected by electron-conducting bond systems (Garten and Weiss, 1957). The nature of these surface functional groups is determined by the method of activation and the carbon source material.

X-ray diffraction has shown that the atoms of activated carbon take the form of microcrystalline carbon, a structure derived from graphite (Dubinin, 1966). This material consists of graphite-like layers stacked parallel to each other in packets of 3 to 30 layers about 10 to 100 Å thick. A graphitic layer contains sp^2 hybridized carbon atoms joined by σ bonds to three adjacent carbon atoms with the fourth electron of each atom located within p orbitals, which overlap to form π bonds. In microcrystalline carbon, the interlayer spacing is larger than in graphite, and the stacking sequence is perturbed resulting in layer planes tilted with respect to one another (Boehm and Coughlin, 1964). The layers are held together by relatively weak van der Waals forces as well as by disorganized, tetrahedrally bonded carbon crosslinking different layers. Also, foreign atoms are always present, usually at the edges of the crystallites to form functional groups, or incorporated within the graphitic layers forming "heterocyclic" ring systems (Dubinin, 1966). The

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"free valences" at the edges of the graphitic layer planes of micro-crystalline carbon are very reactive and form compounds with any suitable foreign atoms present. Thus, surface groups exist almost exclusively at the layer edges of active carbons, since foreign atoms can be only weakly adsorbed on the basal faces by means of the graphitic π electron system (Garten *et al.*, 1957).

Most important of the surface compounds of carbon are those formed with oxygen, because their presence can greatly alter the sorptive capacity of the active carbon. Surface oxide groups most frequently suggested to be present on active carbons include: carboxyl groups; phenolic hydroxyl groups; quinone-type groups; normal lactones; fluorescein-type lactones; carboxylic acid anhydrides; and cyclic peroxides (Figure 1) (Cookson, 1975).

The presence of oxygen complexes on the surface of active carbons tends to increase surface polarity (Barrer, 1966). Therefore, in aqueous solution, a stronger solvent-active carbon bond must be broken before adsorption of the sorbate can occur. With increased surface polarity, water adsorbs strongly through a hydrogen bonding mechanism resulting in pore constriction or blockage. Excluding any specific oxygen complex-sorbate interaction, increased polarity decreases the quantity of nonpolar sorbate which may be removed from solution. For a polar sorbate, the oxygen complex-sorbate interaction is usually stronger, somewhat compensating for the added energy required to desorb water (Coughlin *et al.*, 1968).

Coughlin and Ezra (1968) found that increased concentration of surface oxides greatly reduced the amount of phenol and nitrobenzene that could be adsorbed from dilute aqueous solutions. Using two different carbons, they found that oxidation reduced the adsorptive capacity for phenol by 50% in one case, and by a factor of 8 in the other. However, with higher initial concentrations of phenol, they found no significant reduction in capacity with increased concentration of surface oxides, although no explanation was presented for this apparent anomaly.

Chemisorbed oxygen and surface polarity can also influence adsorbent selectivity. Kipling (1957) discovered that surface oxygen complexes affected the specificity of sorption from an organic, binary liquid solution, and Kipling and Shooter (1966) reported that surface oxides prevent organic iodine molecules from adsorbing to active carbon. In general, it has been demonstrated that relatively polar sorbates, and those that naturally tend to bond with oxygen show the greatest affinity for carbons with extensive surface oxygen complexes.

Factors Associated With The Adsorbate

Organic functional group, molecular weight, extent of skeletal branching, polarity, and aqueous solubility are adsorbate characteristics most influential on the adsorption mechanism. The single most important characteristic in determining amenability of organic compounds to active carbon adsorption is aqueous solubility. Aqueous solubility is an expression of other adsorbate characteristics, and thus provides the simplest, most valid means of adsorbate classification. Keller and Snyder

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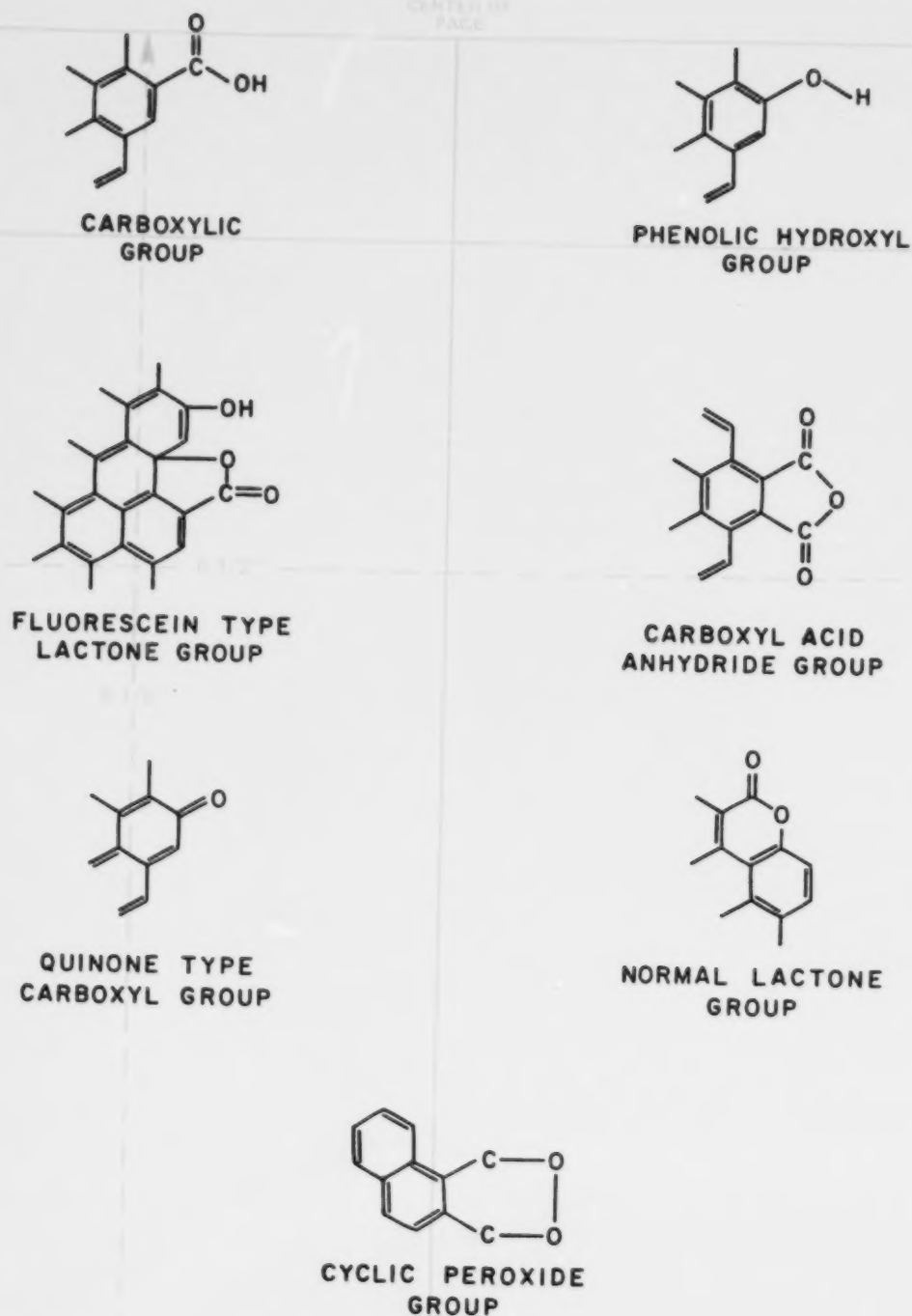


Figure 1. Surface oxide functional groups frequently found on active carbons. (Modified from Cookson, 1975)

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(1971) have attempted to further define the relationship between adsorptive capacity and solubility through use of the liquid-solid solvent strength parameter. Although this parameter provides valuable information in chromatographic systems, its applicability to active carbon chemistry is severely limited.

Adsorbate classification based on the solubility parameter has a thermodynamic basis and wide applicability. Giusti et al. (1974) investigated 93 organic solutes representing 10 different functional groups commonly found in petrochemical wastes. The study showed without exception, that as aqueous solubility decreases, adsorptive capacity increases. This relationship held true not only for decreasing solubility of compounds within a functional group, but also for decreasing solubility between functional groups. These investigators found that for molecules containing four or less carbon atoms, amenability to carbon sorption decreases as follows: undissociated organic acids > aldehydes > esters > ketones > alcohols > glycols. Similarly, for molecules with greater than four carbon atoms the scheme becomes: polynuclear aromatic hydrocarbons > undissociated organic acids > aldehydes > alcohols > esters > ketones > glycols. A more detailed summary of their work pertaining to the relationship between adsorbate characteristics and adsorptive capacity is presented in Table 2.

Other adsorbate characteristics also exhibit well established trends, and are closely tied to solubility. Organic sorbates within a given functional group show increasing adsorptive capacity as molecular weight increases. Adamson (1967) reported data for a polar solvent and fatty acids, verifying Traube's rule that adsorption increases as a homologous series is ascended.

Two other adsorbate parameters influence carbon capacity: branching within the carbon skeleton of adsorbate molecules, and sorbate polarity. Using selected pesticides and sulfonated organics, Morris and Weber (1966) have shown that increasing the extent of skeletal branching serves to decrease adsorptive capacity for otherwise similar molecules. These findings have been supported by Al-Bahrani and Martin (1976) and Giusti et al. (1974) using alcohols and ketones. Similarly, although adsorbate polarity is related to aqueous solubility, for organic molecules of essentially equal solubility, adsorptive capacity is enhanced for the least polar molecule (Al-Bahrani and Martin, 1976).

Factors Associated With The Aqueous System

The solvent surrounding the adsorbent and adsorbate molecules is the third component of the adsorption mechanism. Solution pH, matrix complexity, dissolved solids and temperature are aqueous system characteristics which influence adsorption on active carbons. Temperature is an important parameter in batch, equilibrium systems, but is of little consequence in continuous-flow applications because of the difference in sorption kinetics. Adsorption reactions are exothermic, so adsorptive capacity decreases with increasing temperature. However, in continuous-flow columns, the kinetics of adsorption increase with rising temperature, so moderate temperature variations have no effect on the

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TABLE 2. RELATIONSHIPS BETWEEN ADSORBATE PARAMETERS AND AMENABILITY TO CARBON SORPTION

Functional Group	Relative Polarity	Relative Solubility	MW ⁽²⁾	Skeletal Branching	Amenability to Carbon Sorption
Alcohol	Very	Very	X	X	Poor
Aldehyde	Polar-Very	Soluble	X	X	Poor
Amine	Polar-Very	Very	X	X	Poor
Polynuclear Aromatics	Nonpolar	Insoluble	X	Not Applicable	Excellent
Pyridines	Slightly	Soluble	X	X	Good
Esters	Slightly	Slight-Sol	X	X	Fair-Good
Ethers	Slightly-Non	Slightly	X	X	Good-Excellent
Halogenated HC's	Polar-Non	Slight-Sol	X	X	Fair-Excellent
Glycols	Polar	Very	X	X	Poor-Good
Ketones	Slight-Polar	Soluble	X	X	Poor-Fair
Organic Acids	Polar	Soluble	X	X	Good-Excellent

- (1) Adapted From Guisti et al. (1974).
 (2) X indicates carbon affinity increases with increasing molecular weight.
 (3) X indicates carbon affinity decreases with increased skeletal branching.

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breakthrough curve (Weber and Keinath, 1967).

Dissolved solids can effect the adsorption of ionized organic molecules by affecting changes in surface polarity of active carbons, but they exert no influence on neutral species. Snoeyink *et al.* (1969) studied the effect of dissolved solids on the adsorption of phenols from aqueous solution. At pH 2.0, where phenol exists solely as the neutral specie, they found no capacity difference between solutions containing no NaCl and those containing up to 2 moles/liter. Studies of phenol sorption at pH 10.0 where the ionic specie predominates, indicated a significant "salt effect". Adsorption capacity was greatly enhanced in NaCl matrices ≥ 1.0 M, but capacities were not significantly different in all NaCl solutions less than 1.0 M. Since dissolved solids show no effect on neutral organics, and only enhance adsorption of ionic species at concentrations ≥ 1.0 M, the influence would be minimal in most wastewater applications.

Solution pH and matrix complexity are much more important parameters in wastewater treatment systems. The effect of solution pH is manifested in two components of the adsorption mechanism; the chemical characteristics of the carbon surface, and the extent of dissociation for ionizable adsorbate species. Ward and Getzin (1970) observed that decreasing the solution pH served to increase the adsorptive capacity of aromatic acids, with capacity reaching a maximum near $\text{pH}=\text{pK}_a$. These findings were confirmed by Murin and Snoeyink (1979) using substituted phenols and humic acids. They felt that increased capacity was due not only to an increase in the molecular-ionic ratio, but also because of an enhanced specific ion adsorption resulting from an alteration of the carbon surface properties. Because of the existence of ion-exchange groups at the carbon surface, electrolytes in solution may interact with the carbon to influence its behavior as an adsorbent. Weber and Morris (1964) have shown that the hydrogen ion activity of a solution affects both the rate and capacity for adsorption of negatively charged sulfonated alkylbenzene from aqueous solution. They interpreted the results as indicating that decreasing solution pH led to an increasing association of the hydronium ion with negatively charged surface functional groups. This association results in neutralized electrostatic repulsive forces which allows the charged organic species to migrate through the pore spaces and be adsorbed at inner surface sites more easily. In the case of organics susceptible to ionization, pH conditions yielding the highest undissociated state offer the most ideal conditions for adsorption.

Although the effect of pH is greatest on ionic molecules, Coughlin (1968) noted that pH also affects the capacity of certain neutral species. Using alcohols not susceptible to ionization, he found that increasing solution pH resulted in increased carbon capacity. He suggested two possible mechanisms to explain this phenomena: higher pH may result in formation of higher molecular weight condensation products which are more readily adsorbed than precursor molecules; or, it may serve to neutralize surface oxides making previously blocked micropores available for adsorption.

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Due to the highly complex nature of wastewater streams, matrix effects are particularly important in wastewater treatment applications. In multiple solute systems, each solute potentially adversely affects both

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the rate of adsorption and the adsorbent capacity for the other solutes present. As matrix complexity increases, solute interactions and competition for available adsorption sites become continually more rigorous, and capacity for any given component is further suppressed. The nature and intensity of the interactions is determined by the number of different adsorbates present, the type of adsorbate molecules, adsorbent characteristics, relative concentration levels, and other aqueous system parameters such as pH.

In multiple component systems, adsorption is controlled by solute-solute and solute-adsorbent interactions including specificity, repulsion, and competition. Competition is the most prevalent interaction, resulting in lowered adsorptive capacity for all components. The degree of mutual inhibition of competing adsorbates is related to the relative size of the adsorbates, relative adsorbent affinities, and the relative concentration of each of the competing solutes (Weber and Morris, 1964). Adsorbates which exhibit greater carbon affinity will suppress the adsorptive capacity of lower affinity components substantially, but the opposite effect is minimal. In a bisolute system of phenol and dodecyl benzene sulfate (DBS), Weber and Morris (1964) found that the presence of DBS suppressed the equilibrium capacity of phenol by approximately 30%, but DBS capacity was reduced by less than 10%. A possible explanation may be a function of relative molecular size. Although the smaller phenol molecule has a high effective rate of diffusion, a DBS molecule once having entered a pore of nearly molecular diameter may effectively block most of the cross-sectional area of that pore, thus retarding the intraparticle transport of smaller molecules entering subsequently. Weber and Keinath (1967) observed similar effects on mass transfer rates in three and four component systems. When using three solutes of roughly equal molecular size, they discovered that although the capacity of each was suppressed somewhat, the rates of mass transfer were the same as those in single solute systems. However, when these three solutes were used in a system containing a fourth, much larger solute, the mass transfer rates of the original three components were significantly suppressed.

If the relative magnitude of adsorbate-adsorbent affinity becomes large enough, the high affinity component can even replace low affinity molecules previously adsorbed. This phenomena has been demonstrated in column studies by Baker (1964) where the adsorption of n-amyl acetate caused the desorption of considerable amounts of n-butanol. The n-butanol appearing in the column effluent reached a level of over 50% in excess of the influent n-butanol concentration.

The relative concentration of adsorbate species also plays a major role in competition for adsorption sites. Results from equilibrium adsorption studies indicate that an adsorbate can compete more successfully when its concentration relative to other competing components is increased. Alteration of component concentrations can even lead to changes in system domination as evidenced by data from studies of Murin and Snoeyink, (1979) using chlorinated phenols in bisolute systems (Table 3).

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TABLE 3. CONCENTRATION EFFECTS ON COMPETITIVE ADSORPTION IN BATCH REACTORS⁽¹⁾

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Initial DCP ⁽²⁾	Conc. (μ M)	Initial TCP ⁽³⁾	Conc. (μ M)	Ratio DCP TCP	Avg. Reduction ⁽⁴⁾ in DCP Capacity	Avg. Reduction ⁽⁴⁾ in TCP Capacity
40.4		54.5		0.74	21%	28%
47.1		14.6		3.23	15%	54%
16.6		105.3		0.16	20%	18%

(1) Adapted from Murin and Snoeyink (1979).

(2) DCP = 2,4 -dichlorophenol.

(3) TCP = 2,4,6-trichlorophenol.

(4) Reduction in Capacity = $\{[(\text{capacity in single solute system}) - (\text{capacity in bisolute system})] / (\text{capacity in single solute system})\}$.

Although competition among solutes for available adsorption sites occurs on the majority of the carbon surface, some portion of the surface contains sites so specific that competition is virtually excluded. Solution pH and adsorbent characteristics are the primary forces that determine the extent of this adsorption because non-competitive adsorption is believed to be limited to ionic species. Working with phenol and DBS, Weber and Morris (1964) observed that the combined adsorptive capacity was greater than the capacity of either component in single solute systems. This led them to conclude that the solutes were not competing exclusively for the same sites, but rather some adsorption was occurring at sites specific for one or both solutes. Similar results were obtained by Jain and Snoeyink (1973) using bisolute systems of substituted phenols. They described three different adsorptive mechanisms operating simultaneously: adsorption with equal competition for adsorption sites on the majority of the carbon surface, adsorption of each of the two species on different kinds of sites with only minimal competition, and competitive adsorption of organic anions with electrostatic repulsive forces between adsorbed species.

Adsorption of organic species without competition can be explained in terms of adsorbent surface characteristics and adsorbate size. Site specificity can result from the nature of surface functional groups which can only react with adsorbates containing appropriate functional groups, or it may result from the accessibility of certain pores to only certain adsorbates, with exclusion of others on the basis of molecular size.

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ADSORPTION IN FIXED-BED, CONTINUOUS FLOW CARBON SYSTEMS

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Adsorption Dynamics

Most of the studies on the adsorptive phenomena of activated carbon have been performed with batch adsorption systems. However, batch systems are not practical for most wastewater treatment applications, so fixed-bed adsorbers are the process of choice. The principal advantages of fixed-bed adsorbers are ease of process control, more efficient carbon use, and the ability to regenerate spent carbon for reuse. Fixed-bed adsorbers utilize cylindrical columns packed with granular activated, carbon ranging in size from 8-40 mesh. Depending upon the particular application, carbon columns may be used individually, aligned in series, or aligned in parallel. Carbon adsorption may be used at a number of positions within the treatment process, but generally the final effluent from biological or physical-chemical treatment is passed through the columns for removal of trace organics prior to discharge. With this method of carbon utilization, adsorption parameters discussed previously are applicable, although the magnitude of influence will vary. Additional operational parameters must also be considered to optimize performance.

The major difference between batch and continuous flow systems is the amount of time the adsorbate solution remains in contact with the carbon. In batch systems, the carbon adsorbent is placed into a vessel containing a solution of adsorbate molecules and agitated continuously for a period of time presumably long enough to allow the concentration of adsorbed solute to attain equilibrium with the solution bulk. Equilibrium periods ranging from 24 hours to 33 days have been used in batch studies (Snoeyink et al., 1969). Because of the long contact times relative to those practical in wastewater treatment, adsorption kinetics are significantly different, and results obtained from traditional batch studies are of limited value in predicting quantitative behavior in columnar systems.

The major difference in adsorption kinetics between the two systems is the role of intraparticle adsorption within the carbon pore structure. Before adsorption can occur within the pore structure, adsorbate molecules must first be adsorbed on the external carbon surface and subsequently transported inward. In batch systems, the long contact times allow a substantial amount of adsorption to occur within the pore structure and intraparticle transport becomes the rate limiting step. However, with columnar flow the rate of adsorbate uptake is controlled by film transport at the external carbon surface, and the rate of mass transfer is dependent upon film transport rather than intraparticle transport (Weber and Keinath, 1967). Intraparticle transport emerges as a rate controlling mechanism only very late in column operation, near complete breakthrough, and is thus of much less importance. This difference in mass transfer may result in substantially lower carbon capacity in columnar systems, particularly for lower affinity solutes, and affects changes in other adsorptive phenomena such as competition and selectivity. Guisti et al. (1974), using single solute systems, found the ultimate adsorptive capacity for methyl ethyl ketone and butyraldehyde to be reduced by 17%

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and 13%, respectively, when run in continuous flow systems.

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Operational Parameters In Fixed-Bed Reactors

Operational parameters suggested as being critical in fixed-bed contactors include: surface loading rate; linear velocity; influent concentration; and, carbon contact time. These parameters are all inter-related, but in terms of capacity and adsorption efficiency, surface loading rate and linear velocity appear to have little influence. Zogorski and Faust (1976) studied the effect of loading and velocity in columnar systems using 2,4-dichlorophenol as the adsorbate. Their experiments were designed so that empty bed contact time (EBCT) remained constant by varying the depth of adsorbent in each column. The surface loading rates used were 82, 155, 286, and 396 liters/min./m², corresponding to linear velocities of 12, 24, 46, and 67 cm/min, respectively. They found that the rate of mass transfer and height of the mass transfer zone were increased with increasing flow rate, but the adsorptive capacities were essentially unchanged. These observations were verified in a pilot-scale study conducted by the USEPA on removal of trihalomethanes from drinking water (Symons, 1978). Using a fixed retention time of 7.5 minutes and varying the surface loading rate from 122 - 163 liters/min./m², they observed no difference in the shape of the breakthrough curve or the carbon capacity for chloroform. Thus it is the carbon contact time which is the most important parameter in determining adsorption efficiency.

The complex-hydraulics of fluid flow through porous media prevents an accurate determination of solution residence time in carbon columns, so empty bed contact time has become the conventional parameter. EBCT is simply the carbon bed volume when empty, divided by the solution flow rate through the bed. The strength of adsorbate - adsorbent affinity and extent of competition determine the contact time required for optimal removal; consequently, this time varies with each system. Extensive tests by the Calgon Corporation with a wide variety of organics indicate that EBCT's of 5-30 minutes will achieve 84-100% of the adsorptive potential of all compounds tested in DIW matrices (Hansen, 1978). Contact times of less than five minutes do not allow sufficient time for efficient mass transfer to occur, and times in excess of thirty minutes result in such small efficiency increases that they are not practical. Since the vast majority of non-volatile toxic organic contaminants are readily adsorbable, contact times of 7-20 minutes appear to be most efficient in wastewater matrices. However, because of the highly variable nature of such matrices, bench-scale adsorption tests should be performed on the specific wastewater to be treated in order to optimize removal.

Several investigations have shown that as influent concentration increases, adsorptive capacity increases. Weber and Keinath (1964) examined this phenomenon using sulfonated alkylbenzene over an influent concentration range of 13.3-73.3 μ M. They found mass transfer coefficients to be equal over this concentration range, but mass transfer rate and carbon capacity to increase linearly with influent concentration. As influent concentration increases, the gradient between the solution bulk

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and the adsorbent surface increases, so the driving force for mass transfer becomes greater. As a result, the mass transfer rate is increased, and film diffusion remains rate limiting for shorter periods of time because the external surface becomes saturated more rapidly.

In a similar study utilizing 2,4-dichlorophenol, Zogorski and Faust (1976) concluded that although the rate of mass transfer and capacity are greater with increased influent concentration, the rate of adsorption is slower. This conclusion was based on the finding that the height of the mass transfer zone is increased as concentration increases. The height of the mass transfer zone is a representation of the length of column required to affect 100% removal of a given unit of adsorbate solution. Thus, at high concentration more adsorbate molecules are present, so the rate at which solute molecules are transferred to the adsorbent surface is faster, but the mass of carbon required to remove a given amount is greater. Zorogski and Faust (1976) also noted that at higher influent concentration the volume treated, or time until initial breakthrough occurs is shorter, so regeneration is required more frequently even though carbon capacity is greater.

FIXED-BED REACTOR PERFORMANCE FOR REMOVAL OF SPECIFIC ORGANICS

Drinking Water Treatment Applications

Research emphasis on removal of specific organic pollutants by fixed-bed GAC reactors has been focused primarily on the treatment of drinking waters. Organic pollutant control in drinking waters has received priority for several reasons including: results of national surveys of 113 finished drinking water supplies which revealed the presence of over 125 synthetic organic pollutants (Fed. Register, 2-9-78); mounting toxicological evidence indicating significant danger from chronic exposure to such pollutants; and, drinking water is the most direct route of exposure to synthetic organic toxicants. These factors resulted in stimulated research on organic pollution control in the early 1970's, and culminated with the issuance of amendments to the National Interim Primary Drinking Water Regulations in 1978 (Fed. Register, 2-9-78). These amendments, which were aimed directly at control of synthetic organic pollutants, established maximum contaminant levels (MCL's) for trihalomethanes (THM's) and mandated the use of GAC as the technology for removal of these contaminants. Investigations undertaken in developing the basis for the 1978 amendments generated some of the best data available on removal of specific organics by GAC. A review of these results, and those completed since that time, are summarized below.

Trihalomethanes

THM's and their precursors (naturally occurring organics, generally humic and fulvic acids) have been the subject of the most intensive investigation of any class of organic compounds. THM's have been the research and regulatory focal point because results of the 1975 National Organics Reconnaissance Survey indicated they were the most ubiquitous species found in drinking waters, and they are particularly toxic (Symons

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et al., 1975). The precursors are of interest because the prevalent use of chlorine for disinfection purposes results in production of THM's as oxidation products of the chlorine-humic/fulvic acid reaction. Because no direct measurement exists for THM precursors, the degree of precursor removal is evaluated in terms of trihalomethane formation potential (THMFP) (Steven and Symons, 1977). The process involves comparing THM concentrations upon chlorination of an untreated control water to data collected on a treated water after similar chlorination and storage. GAC studies have addressed both THM and THMFP removal efficiency.

Pilot and full-scale studies on THMFP removal by GAC columns indicate that efficiency is variable and highly dependent upon the nature of natural organics present in the source water. Results of studies on THMFP removal at full-scale treatment plants in southern Florida (ground water source) and southern Louisiana (Mississippi River water source) indicate that initial efficiencies of 95% are rapidly reduced to less than 50% in 1-8 weeks of operation (Symons, 1978). However, although removal efficiencies were quickly reduced to 30-50%, this level was maintained for the duration of the study period (about 25 weeks). Similar results have been reported by Glaze et al. (1981) for a pilot system treating reservoir surface waters where initial THMFP breakthrough was observed in 6-10 weeks, but complete breakthrough had not occurred after a full year of operation. Results of a study by Lee and Snoeyink (1980) further support the phenomenon of rapid initial breakthrough, followed by a prolonged period of steady-state adsorption of THMFP components. These findings suggest that although efficient THMFP removal is short-lived, fair removal (30-40%) can be afforded for long periods of time without regeneration.

The EPA has conducted several pilot scale studies to evaluate the effectiveness of GAC for trihalomethane removal from drinking waters. In one such investigation, two GAC columns were operated in parallel to observe the removal of chloroform, bromodichloromethane, dibromochloromethane, and bromoform from Cincinnati, Ohio, tap water (Symons, 1976). After four weeks operation (at 81.5 l/m² loading) the ability of the GAC to remove chloroform and bromodichloromethane was severely reduced. Dibromochloromethane was removed to below the detection limit throughout the four-week study period, but no data could be obtained for bromoform, as it never appeared in the column influent. Subsequent studies were undertaken to examine THM/haloform removal over a longer period of time (Symons, 1978). Results show that chloroform was reduced 90% or more for the first three weeks of operation (10-minute EBCT) and then breakthrough was steady until the adsorber was exhausted at about the ninth or tenth week. The THM species containing bromine however, were effectively reduced by the GAC bed for over 30 weeks of operation.

These findings were consistent with results of the studies conducted on Florida groundwater and Mississippi River water which revealed that chloroform was the least effectively adsorbed THM, while the brominated species were most efficiently removed (Symons, 1978). At the lower Mississippi River water treatment plant, chloroform began to appear consistently in the GAC effluent after the fifth week of operation, and subsequent operation indicated adsorption-desorption cycles began after the 13th week. Similar results have been reported by Rook (1976) for a

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raw surface water spiked with chloroform and bromoform at the low mg/l range. Using a 12 minute EBCT, breakthrough times were 7 days for chloroform and 22 days for bromoform.

In summary, available data indicate that although GAC adsorption can be an effective technique for THM control in drinking waters, two distinct disadvantages must be considered. The relatively weak carbon affinity for THM's, particularly chloroform, results in: 1) low adsorptive capacity which leads to rapid breakthrough making economic feasibility questionable; and, 2) a significant potential for desorption requiring careful column monitoring. However, the other approach to THM control, adsorptive removal of precursor compounds, appears to be a more promising alternative. With this approach, sustained periods of adequate removal (30-40%) have been demonstrated, even though initial breakthrough is quite rapid. Used in conjunction with efficient process control and chlorination practices, this technique appears capable of keeping THM concentrations below the current criterion level.

Other Volatile Organics

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Several investigations have examined the adsorption of carbon tetrachloride and related contaminants. Two such studies have been conducted by the EPA on GAC removal of carbon tetrachloride from Cincinnati, Ohio tap water (Symons, 1978). In the first of these investigations, monitoring for carbon tetrachloride began after the GAC columns had been in service for two months in connection with a THM study. Table 4 depicts the GAC performance over the last eight months of the study period. Even though the bed had been in service for two months, the GAC was quite effective for five months, affecting complete removal for the first three months. However, when the influent level fell to below detection during the last four months of operation, desorption of carbon tetrachloride was observed.

TABLE 4. GAC ADSORPTION OF CARBON TETRACHLORIDE⁽¹⁾

	SERVICE TIME (Months)								
	3	4	5	6	7	8	9	10	11
Monthly Average Influent Conc.(µg/l)	5	8	13	15	48	ND ⁽²⁾	ND	ND	ND
Monthly Average Effluent Conc.(µg/l)	ND	ND	ND	<6	14	16	13	6	6

(1) Adsorption from Cincinnati, Ohio, tap water with a 10-minute EBCT. Data from Symons, 1978.

(2) ND = none detected.

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In the second investigation, carbon tetrachloride monitoring was begun immediately after a new column of virgin GAC was put on line (EBCT = 11 minutes). Results from this study show adsorptive phenomena very similar to those obtained from the previous one. During the first 7 weeks of operation, the GAC column was very efficient, reducing high influent concentrations (10-60 PPB) to less than 1.0 PPB. However, after 8 or 9 weeks the influent level fell below the detection limit (0.1 PPB) and the desorption cycle emerged. This desorption pattern, which was subsequently monitored every 6 weeks, continued for the duration of the 11-month study.

Results from three particularly informative studies on GAC adsorption of volatile organics are summarized in Tables 5-7 below.

TABLE 5. VOLATILE ORGANICS REMOVAL FROM NEW ENGLAND GROUND WATER BY GAC⁽¹⁾

Contaminant	Influent Conc. Range (µg/l)	Average Effluent Conc. (µg/l)		
		0-4 Weeks	4-8 Weeks	8-12 Weeks
1,1,1-trichloroethane	10.9 - 36.7	ND	ND	0.4
trichloroethylene	1.9 - 7.7	ND	0.1	0.1
tetrachloroethylene	0.1 - 16.9	ND	0.1	0.1
1,1-dichloroethane	not given	ND	0.7	not given
cis-1,2-dichloroethylene	not given	ND	ND	ND

(1) GAC columns treating raw ground water with a 10-minute EBCT, data adapted from Symons (1978).

(2) ND = none detected.

Adsorption patterns observed for these compounds closely reflect THM adsorption trends, and similar conclusions can thus be inferred from these data. GAC adsorption is generally an effective control technique for these pollutants, but relatively low carbon affinity limits useful bed life and results in significant potential for desorption.

Other Synthetic Organic Contaminants

Using two 76 liter per minute GAC columns, Robeck et al. (1965) investigated the removal of selected pesticides from sand filtered river water. The two columns were operated in series, with the first column exhausted for COD removal prior to initiation of the test. Spiked river

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TABLE 6. REMOVAL OF VOLATILE ORGANICS FROM TREATED DRINKING WATER BY GAC⁽¹⁾

GAC Service Time (weeks)	GAC Effluent Concentration (µg/l)			
	Benzene	1,2-dichloroethane	Trichloroethylene	Toluene
1	0.1	0.2	ND	0.1
2	ND ⁽²⁾	ND	ND	ND
3	ND	0.1	ND	ND
4	ND	ND	ND	ND
5	0.1	0.3	ND	0.1
6	ND	1.1	ND	ND
7	ND	0.7	ND	ND
8	ND	0.8	ND	ND
9	ND	1.3	0.4	ND
10	ND	1.4	ND	ND
11	0.1	1.0	ND	0.2
12	ND	2.0	ND	ND
13	ND	3.5	ND	ND
15	ND	4.5	ND	ND
20	ND	10.1	ND	ND
25	ND	9.4	ND	ND
Avg. Influent Conc. (µg/l)	0.3	8.0	0.3	0.2
Range Influent Conc. (µg/l)	ND-2.1	1.2-23.7	ND-0.9	ND-0.9

- (1) GAC columns received coagulated, settled, softened, and sand filtered Mississippi River source water, with a 25 minute EBCT. Data adapted from Symons (1978).
 (2) ND = None detected.

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TABLE 7. REMOVAL OF VOLATILE ORGANICS FROM FLORIDA GROUND WATER BY GAC ⁽¹⁾

Influent ⁽³⁾ Conc. (µg/l)	A	B	C	D	E	F	G	H	I	J
	1.3	0.3	29.0	0.13	0.06	0.19	0.11	1.1	0.8	0.11
	GAC Effluent Concentration (µg/l) ⁽²⁾									
GAC Service Time (weeks)										
1	ND ⁽⁴⁾	ND	0.18	ND	0.006	ND	ND	ND	- ⁽⁵⁾	0.003
2	ND	ND	0.20	ND	0.004	ND	ND	0.002	-	ND
3	0.002	0.02	2.7	0.002	0.001	0.01	ND	ND	-	0.003
4	ND	0.08	4.2	ND	0.002	ND	ND	ND	-	ND
5	0.002	0.007	7.8	ND	ND	ND	ND	ND	-	0.006
6	ND	0.013	5.3	ND	ND	ND	ND	ND	-	ND
7	0.002	0.015	12.0	ND	ND	ND	ND	ND	-	0.002
8	0.04	0.02	18.0	ND	ND	0.001	ND	ND	-	0.003
9	0.02	0.03	17.3	ND	ND	ND	ND	ND	-	0.003
10	0.05	0.04	21.6	ND	ND	ND	ND	ND	-	0.002
11	0.07	0.10	10.2	0.01	ND	ND	ND	ND	-	ND
12	0.07	0.02	18.7	0.006	ND	ND	ND	ND	-	0.03
13	0.66	0.32	25.7	0.06	ND	ND	ND	ND	0.79	0.01
14	0.45	0.17	30.4	0.07	ND	ND	ND	ND	0.70	0.10
15	0.90	0.38	23.3	0.05	ND	ND	ND	ND	0.81	0.06
16	0.76	0.34	21.9	0.06	ND	ND	ND	ND	0.75	0.05
17	0.60	0.23	21.3	0.028	ND	ND	ND	ND	0.78	ND

(1) Data adapted from Symons (1978). EBCT = 6.2 minutes.

(2) Compound codes are as follows:

A = trans - 1,2-dichloroethylene

F = chlorobenzene

B = 1,1-dichloroethane

G = p-chlorotoluene

C = cis-1,2-dichloroethylene

H = m,p,o-dichlorobenzene

D = trichloroethylene

I = $\overline{\text{vinyl}}$ chloride

E = tetrachloroethylene

J = 1,1,1-trichloroethane +
1,2-dichloroethane +
carbon tetrachloride

(3) Influent concentrations are average values for the 17-week period.

(4) ND = none detected.

(5) - = not determined.

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water was applied to the exhausted column, and the effluent from it applied to a second fresh column. With influent concentrations of dieldrin as high as 4.3 $\mu\text{g/l}$, the effluent level from the first column was reduced to 0.3 $\mu\text{g/l}$. In spite of sudden increases in influent COD from the river water, the dieldrin concentration in effluents from the second carbon column reached levels as low as 0.05 $\mu\text{g/l}$ routinely, and often below the detection limit of 0.01 $\mu\text{g/l}$. They concluded that preferential adsorption of pesticides by GAC columns afforded excellent protection in drinking water applications.

However, contradictory results have been reported by Richard *et al.* (1976) for GAC columns receiving Mississippi River water influent. Analysis of influent samples showed concentrations of atrazine, DDE, and dieldrin of 0.33, <0.0005, and <0.0005 $\mu\text{g/l}$, respectively, while carbon column effluent levels were 0.46, 0.002, and 0.001 $\mu\text{g/l}$, respectively. Results from this study (which indicate desorption was occurring) must be considered inconclusive however, because of several experimental shortcomings. The two most significant factors were that the extent of column exhaustion was unknown, and poor sampling/analytical techniques were used. This latter factor makes it impossible to determine if column effluent levels were actually higher than influent concentrations.

In another EPA study, Robeck (1975) examined GAC removal of naphthalene spiked into Cincinnati, Ohio, tap water. Column influent (spiked at 30 $\mu\text{g/l}$) was loaded at 82 liters/min/ m^2 , resulting in a 17-minute EBCT. After 7 months of operation, the nonvolatile total organic carbon 50% removal front had penetrated the first 51 cm of the carbon bed, while the 50% removal front for naphthalene moved only about 5 cm. The data suggest that GAC columns can effectively remove low solubility, high affinity contaminants (such as pesticides and PNA's) for long periods of time with little loss in efficiency.

Dostal *et al.* (1965) investigated GAC removal of seven organic compounds of industrial origin from Kanawha River water. These compounds, which were responsible for odor problems, were present at 10-100 $\mu\text{g/l}$ in the heavily polluted river water, and included: bis (2-chloroisopropyl) ether; bis (2-chloroethyl) ether; 2-ethylhexanol; methylbenzyl alcohol; acetophenone; isophorone; and, tetralin. They found that initially all seven compounds were removed to below detection limits by fresh activated carbon. After 40 days of operation, all of the compounds except acetophenone had penetrated the GAC bed to a depth equal to an EBCT of 7.6 minutes. With an additional 3.6 minutes of contact time, all seven compounds were reduced to below the detection limit, but an additional component, ethyl benzene, was discovered to be penetrating to a depth equal to 15 minutes EBCT.

Thus, available data indicate that not only is fixed bed GAC an effective technology for removal of a broad spectrum of organic contaminants, but also quite effective in relatively complex matrices such as the raw river water source used by Dostal *et al.* (1965). These findings (particularly the broad spectrum application) led the EPA to recommend the use of GAC as the preferred technique for control of synthetic organic contaminants in drinking water treatment.

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Wastewater Treatment Applications

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Relatively little data is available on GAC removal of specific organic contaminants from wastewater matrices. Of that available, the most thorough investigations have been performed in conjunction with evaluations of wastewater reclamation for ground water recharge. The most notable of these studies have been conducted at Water Factory 21 in Orange County, California, and at two pilot plants in Pretoria, South Africa. In all three cases, influent to these advanced treatment facilities is a secondarily (biologically) treated combined domestic/industrial wastewater. The advanced treatment scheme is also common to all three plants, and entails: 1)chemical clarification; 2)ammonia stripping; 3)recarbonation; 4)dual media filtration; 5)chlorination; 6)GAC adsorption; 7)chlorination; and, 8)discharge. A summary of GAC performance for removal of specific pollutants at these three facilities is presented in Tables 8 and 8A.

Although these data are quite comprehensive in terms of GAC removal efficiency for a variety of specific synthetic organic pollutants, they are of somewhat limited value in that they only indicate average removals over a relatively long time period. This type of data provides no information on carbon capacity, or the progressive breakthrough of these compounds with time. Breakthrough curves (plots of effluent concentration vs. run time) are most informative, as they indicate the point at which toxicants begin to appear in column effluents, and also effluent levels upon subsequent column operation. Breakthrough curves are thus valuable tools for predicting effective carbon bed life or regeneration requirements, and therefore can be used for assessing economic considerations also. Breakthrough curves have been established for several common organic contaminants in drinking water applications, but very little data exists on the shape of breakthrough curves for adsorption of specific pollutants from wastewater treatment applications.

Summary Of Available Literature

In summary, the mechanism of adsorption from aqueous solution is well understood for static adsorption systems (batch reactors) treating relatively simple water matrices. However, two major problem areas exist which inhibit accurate prediction of carbon performance in practical field applications. The first concerns differences in adsorptive mechanisms between batch reactors and continuous flow adsorbers. This poses a problem because the vast majority of the adsorption theory and predictive models have been developed from studies of adsorption in batch reactors, yet it has not been definitively shown that adsorptive phenomena are equivalent to those occurring in continuous flow systems. Therefore, since differences likely exist, and the significance of such differences is unknown, many models based on batch adsorption data have proven to be of limited value in predicting carbon performance in actual application.

The inability to adequately describe adsorption phenomena from complex water matrices constitutes the other major shortcoming in

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TABLE 8. GAC PERFORMANCE AT WATER FACTORY - 21⁽¹⁾

Group/Compound	GAC Influent Conc. (µg/l)	GAC Effluent Conc. (µg/l)	GAC Removal Efficiency (%)
THM's			
Chloroform	19	9.3	51
Bromodichloromethane	8.8	2.1	76
Dibromochloromethane	4.0	0.6	85
Bromoform	1.8	0.2	89
Other Highly Volatiles			
Dichloromethane	3.3	2.6	21
1,1,1-trichloroethane/ CCl ₄	0.08	0.08	0
Trichloroethylene	0.10	0.03	70
Tetrachloroethylene	0.3	0.1	67
Volatile Aromatics			
Ethylbenzene	0.06	0.03	50
Chlorobenzene/ o - xylene	0.10	0.05	50
1,2-dichlorobenzene	0.30	0.06	80
1,3-dichlorobenzene	0.03	0.005	83
1,4-dichlorobenzene	0.03	0.02	33
1,2,4-trichlorobenzene	0.02	0.01	50
Naphthalene	0.11	0.04	64
Other Synthetic Organics			
PCB 1242	0.3 ⁽²⁾	0.2 ⁽²⁾	33
Diethylphthalate	10.9	5.8	47
Dioctylphthalate	1.3	1.4	<0
COD	45 PPM	15 PPM	67
TOC	15 PPM	7.2 PPM	52

- (1) GAC performance (removal efficiencies) calculated from mean influent and effluent levels averaged over an 8-month period. Data adapted from Reinhard *et al.* (1979).
 (2) Concentration values are estimates.

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TABLE 8A. GAC PERFORMANCE AT SOUTH AFRICAN PILOT PLANTS⁽¹⁾

Group/Compound	Treatment Facility	GAC Influent Conc.(µg/l)	GAC Effluent Conc.(µg/l)	GAC Removal Efficiency (%)
Pesticides				
Lindane	1 ⁽²⁾	4	0.07	98
Dieldrin	1	27	0.3	99
Chlordane	1	144	1.4	99
Fenthion	1	1040	ND ⁽³⁾	100
α-BHC	2 ⁽⁴⁾	11.8	ND	100
Atrazine	2	19.2	ND	100
Chlorfenvinphos	2	12.6	ND	100
Endosulfan	2	3.2	ND	100
Dieldrin	2	0.7	ND	100
Phenols				
Phenol	1	72	1.4	98
Trichlorophenol	1	212	6.4	97
Phenol	2	0.2	ND	100
Pentachlorophenol	2	0.3	ND	100
Other Synthetic Organics				
O-nitrotoluene	1	60	4.2	93
Dibutyl Phthalate	1	188	1.9	99
nitrotoluene	2	3.8	ND	100
(bis)chlorethyl ether	2	18	2.2	88

(1) Data adapted from van Rensburg et al. (1979).

(2) Treatment facility 1 = pilot plant at the Stander water reclamation plant in Pretoria, South Africa.

(3) ND = none detected.

(4) Treatment facility 2 = LFB pilot plant in Pretoria, South Africa.

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current adsorption theory. A great deal remains to be learned about both qualitative and quantitative aspects of GAC adsorption from complex matrices where competitive adsorption forces predominate. The complexity of competitive adsorption interactions precludes accurate prediction of carbon performance in both batch and continuous-flow adsorption systems. This problem is compounded by the immense variability in type, concentration, and relative number of organic species found in waters to be treated. Matrix complexity is a particularly significant factor in wastewater treatment applications where hundreds of different organic species may be competing for available adsorption sites.

Practical application of GAC adsorption technology has clearly been best documented in drinking water applications, where it has been shown to be an effective removal technique for a number of organic pollutants. Even in drinking water applications however, little data is available on the shape of breakthrough curves for specific contaminants or on GAC adsorptive capacities. Data availability on breakthrough characteristics of specific organics is even more limited for GAC adsorption from more complex wastewater matrices. It is thus the aim of this study to examine breakthrough characteristics of selected organic toxicants from a secondarily treated industrial wastewater matrix in order to provide more information on competitive adsorption phenomena.

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SECTION 5

EXPERIMENTAL DESIGN

The major objective of this study was to evaluate granular activated carbon column treatment as a means for removal of refractory organic toxicants from secondarily treated combined industrial wastewaters. In addition, the suitability of general parameters, TOC and COD, in monitoring column breakthrough was to be evaluated. A series of bench scale studies utilizing a mass balance approach to assess adsorption characteristics of selected organics spiked into pure and wastewater matrices were designed to accomplish these objectives. Site studies utilizing unspiked combined industrial effluent were designed to apply information gained from the bench scale columns to the assessment of column effectiveness under actual treatment site conditions.

BENCH ADSORPTION STUDIES

Spike Constituent Selection

Polynuclear aromatic hydrocarbons (PNA's), chlorinated hydrocarbons (aliphatic and aromatic), phthalic acid esters, and substituted phenols were selected for use in the various adsorption matrices employed in this study. Representative members of these classes of organic compounds were chosen from the EPA list of "priority pollutants" (Fed. Register, 1-31-78). Selection of specific organic compounds was based on consideration of three general criteria: 1) occurrence; 2) carbon sorption characteristics; and, 3) toxicity/environmental significance. Individual toxicants used in this study are listed in Table 9 below.

Each of these compounds (with the exception of 1,1,2,2-tetrachloroethane) had been previously confirmed to be present in the wastewater matrix to be studied (USEPA, 1979). Within a given class of organics, at least one compound was chosen on the basis of high water solubility. Carbon affinity, and hence adsorptive efficiency, generally decreases with increasing water solubility. Thus, by selecting a relatively high solubility component, results for this compound should be indicative of "worst case" breakthrough for that class of organic solutes.

Finally, selection was based upon factors associated with these

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TABLE 9

ORGANIC TOXICANTS SELECTED FOR CONTINUOUS - FLOW STUDIES

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Semi-volatile Components

Polynuclear Aromatic Hydrocarbons

Acenaphthylene
Phenanthrene

Phthalic Acid Esters

Dimethyl Phthalate
Diethyl Phthalate
Di-n-butyl Phthalate

Phenols

2-chlorophenol
2-nitrophenol
2,4-dimethylphenol
2,4-dichlorophenol
Phenol

Chlorinated Hydrocarbons

1,4-dichlorobenzene
Hexachloroethane

Volatile Components

Chlorinated Hydrocarbons

1,1,2,2-tetrachloroethane

compounds which indicate that they directly, and/or indirectly, pose a significant threat to the quality of human life. Direct effects are those related to deterioration of human health, while indirect include toxic responses in aquatic organisms which threaten the stability of man's food supply. Prominent among the factors which make these organics particularly dangerous are demonstrated carcinogenicity/toxicity, prevalence in industrial effluents, widespread distribution, resistance to conventional wastewater treatment technologies, and persistence in the aquatic environment.

Where data are available, Tables 10 and 11 list important sources of environmental contamination, present data on biodegradation/persistence, and summarize significant biological effects for each compound used in this study. Table 12 presents the final water quality criteria issued by the EPA, where sufficient bioassay data exist to develop such criteria.

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TABLE 10. NATURAL AND ANTHROPOGENIC SOURCES OF ENVIRONMENTAL CONTAMINATION, BIODEGRADABILITY, & PERSISTENCE

Compound	Sources/Occurrence	Industrial Users (1)	Biodegradability/Persistence	Reference (2)
PNA's (as a class)	ubiquitous compounds found in soils, natural waters, and vegetation evidence that PNA's are produced naturally by bacteria and algae as metabolic byproducts levels in raw sewage indicate human excretion of unaltered PNA's or are metabolic byproduct major anthropogenic sources are auto exhaust, energy production from fossil fuel (produced by incomplete combustion of hydrocarbons during high temperature pyrolysis)- petroleum refining, coal tar distillation	manufacturers of dyes, plastics, pesticides, asphalt, & coal tars	extent to which PNA's can be removed by conventional treatment is dependent upon the particular compound-primary sedimentation, activated sludge, and secondary sedimentation can affect 80% removal activated carbon is most effective treatment mechanism-99% lower MW PNA's are partially degraded biologically, but those with MW>anthracene show no detectable biodegradation in long term studies	Borneff & Knute, (1963) *Reichert et al., (1971) Knorr & Schenk, (1968) *Borneff & Fisher, (1961) Borneff & Knute, (1967) *Malaney et al., (1967)
Phthalate Esters				Knorr & Schenk, (1968)
Dimethyl				
Phthalate	organic chemical industry	manufacture of plasticizers, plastics, latex, double-base rocket fuel, rubber	somewhat susceptible to activated sludge treatment, but no specific data available	

(1) Reference: The Merck Index- An encyclopedia of chemicals and drugs, 9th edition.
(2) *Indicates reference used in biodegradability/persistence category.

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TABLE 10. (CONTINUED)

Compound	Sources/Occurrence	Industrial Users (1)	Biodegradability/Persistence	Reference (2)
Diethyl Phthalate	organic chemical industry	manufacture of plasticizers, plastics, insecticidal sprays, wetting agent, food packaging applications, denaturant	somewhat susceptible to activated sludge treatment, but no specific data available	
Di-n-butyl Phthalate	organic chemical industry	manufacture of plasticizers, plastics, double-base rocket fuels, printing ink, insecticides, textile lubricating agent	aerobic degradation in fresh water hydrosoils: 50% after 24 hours incubation	Johnson & Luives, (1975)
Phenols				
2-Chlorophenol	primary occurrence in water and wastewaters is through the reaction of phenol and chlorine disinfectant	topical antiseptic	decomposition rate in aquatic soil suspensions: 14 days for complete disappearance-decomposition by soil microflora > 64 days	*Woodcock, (1971) *Alexander & Lustigan, (1966)
2,4-Dichlorophenol	primary occurrence in water and wastewaters is through the reaction of phenol and chlorine disinfectant		in bacterial culture, 8% degradation in 7 days decomposition rate in aquatic soil suspensions: 7 days for complete disappearance	*Bunch et al., (1967)
2-Nitrophenol	organic chemical industry	manufacture of insecticides, resins, pH indicators	decomposition rate by aquatic soil microflora > 64 days	*Alexander & Lustigan, (1966)

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TABLE 10. (CONTINUED)

Compound	Sources/Occurrence	Industrial Users (1)	Biodegradability/Persistence	Reference (2)
2,4-Dimethyl-phenol	organic chemical industry, coal tar fractionation, & coal processing	manufacture of plastics, resins, disinfectants, solvents, pesticides, rubber, polyethylene oxide	no specific data available	
Phenol	organic chemical industry	manufacture of medically important compounds, resins, disinfectants	decomposition rate in aquatic soil suspensions: 1 day for complete disappearance	*Alexander & Lustigman, (1966)
Chlorinated Hydrocarbons				
1,4-Dichlorobenzene	organic chemical industry	manufacture of moth repellents, insecticides, air deodorizers, pharmaceuticals	200 mg/l degraded by <u>Pseudomonas</u> at 30 °C	*Verschuieren, (1977)
Hexachloroethane	organic chemical industry	manufacture of explosives, fire extinguishing fluids, nitrocellulose solvent, plasticizer for cellulose esters	evaporation from water: 50% at > 2 hours for 1 mg/l solution	*Verschuieren, (1977)
1,1,2,2-Tetrachloroethane	organic chemical industry	manufacture of organic solvents, chlorinated rubber, degreasers, waxes, resins, rust remover, insecticides, herbicides	evaporation from water: 90% at > 2 hours for 1 mg/l solution	*Verschuieren, (1977)

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TABLE 10. SUMMARY OF ADVERSE BIOLOGICAL RESPONSES TO STUDY TOXICANTS

Compound	Biological Response	Organism	Response Level	Reference
PNA's (as a class)	carcinogenicity-many have been proven carcinogens & most are suspect, particularly derivatives of anthracene and pyrene mutagenicity	Mammalia: rat	definitive response levels unavailable	Eisenbud, (1978) McCann et al., (1975)
		Bacteria: <u>Salmonella</u>	0-300 mutations/nM (dependent upon particular PNA tested)	McCann et al., (1975)
Phenanthrene	toxicity	Polychaete: <u>Neanthes arenaceodentata</u>	96 hr TL _m = 0.5 mg/l	Rossi & Neff, (1978)
Acenaphthylene	toxicity	Polychaete: <u>Neanthes arenaceodentata</u>	96 hr TL _m = 0.6 mg/l	Rossi & Neff, (1978)
Phthalate Esters Dimethyl Phthalate	toxicity	Mammalia: rat guinea pig	acute oral LD ₅₀ = 6.9 g/kg acute oral LD ₅₀ = 2.4 g/kg	Patty, (1967) Patty, (1967)
Diethyl Phthalate	inhibition of cell multiplication	Algae: <u>Microcystis aeruginosa</u> Bacteria: <u>Pseudomonas putida</u>	inhibition occurs at > 15 PPM inhibition occurs at > 400 PPM	Verschueren, (1977) Verschueren, (1977)
Di-n-butyl Phthalate	toxicity	Freshwater fish: no specie given Freshwater arthropod: no specie given	acute LC ₅₀ = 310 mg/l acute LC ₅₀ = 36 mg/l	Fed. Register, (7-25-79) Fed. Register, (7-25-79)

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TABLE 11. (CONTINUED)

Compound	Biological Response	Organism	Response Level	Reference
Phenols				
2-Chlorophenol	toxicity	Algae: <u>Scenedesmus</u> Fish: bluegill sunfish	LD ₀ = 60 mg/l TL _m (24-96 hr) = 12-8 mg/l	Jones, (1971) Pickering & Hencherson, (1966)
2,4-Dichlorophenol		Mammalia: rat	acute oral LD ₅₀ = 0.67 g/kg	Patty, (1967)
	Inhibition of cell multiplication	Algae: <u>Microcystis aeruginosa</u>	inhibition occurs at > 2 mg/l	Verschuuren, (1977)
		Bacteria: <u>Pseudomonas putida</u>	inhibition occurs at > 6 mg/l	Verschuuren, (1977)
2-Nitrophenol	toxicity	Algae: <u>Scenedesmus</u> Arthropoda: <u>Daphnia</u>	acute LD ₀ = 36 mg/l acute LD ₀ = 60 mg/l	Verschuuren, (1977) Price et al., (1974)
		Fish: bluegill sunfish	TL _m (24-48 hr) = 67-46 mg/l	Lammering & Burbank, (1960)
2,4-Dimethylphenol	toxicity	Algae: <u>Scenedesmus</u> Arthropoda: <u>Daphnia</u> Fish: trout embryo	acute LD ₀ = 40 mg/l acute LD ₀ = 24 mg/l TL _m (24 hr) = 28 mg/l	Verschuuren, (1977) Price, (1974) Verschuuren, (1977)
Phenol	Inhibition of cell multiplication toxicity	Algae: <u>Microcystis aeruginosa</u> Arthropoda: <u>Daphnia</u> Fish: bluegill sunfish rainbow trout	inhibition occurs at > 46 mg/l acute LD ₀ = 16 mg/l TL _m (24 hr) = 22.7 mg/l 2 hr LD ₀ = 7.3 mg/l	Verschuuren, (1977) Price, (1974) Lammering & Burbank, (1960) Mitrovic, (1968)

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TABLE 11. (CONTINUED)

Compound	Biological Response	Organism	Response Level	Reference
Phenol	toxicity	Mammalia: rat	single dose LD ₅₀ = 0.53 g/kg	Patty, (1967)
Chlorinated Hydrocarbons				
1,4-Dichlorobenzene	toxicity	Fish: no specie given	TL _m (24 hr) = 50 mg/l	Verschueren, (1977)
Hexachloroethane	inhibition of cell multiplication	Bacteria: <u>Pseudomonas</u>	inhibition occurs at > 5 mg/l	Verschueren, (1977)
	toxicity	Mammalia: dog	MLD = 325 mg/kg	Patty, (1967)
1,1,2,2-Tetrachloroethane	toxicity	Mammalia: dog	MLD = 700 mg/kg	Patty, (1967)
		Marine athropod: no specie given	acute LC ₅₀ = 9 mg/l	Fed. Register, (11-28-80)

TABLE 12. ENVIRONMENTAL PROTECTION AGENCY AMBIENT WATER QUALITY CRITERIA (FED. REGISTER, 11-28-80)

Compound	Protection of Freshwater Aquatic Life			Protection of Adverse Effects on Human Health
	Criterion (2)	Chronic Toxicity (1)	Acute Toxicity (1)	
PNA's (as a class)	no criterion	no data	no data	28, 2.8, & 0.28 ng/l (3)
Phthalates (as a class)	no criterion	0.003 mg/l	0.94 mg/l	-----
Dimethyl Phthalate	no criterion	-----	-----	313 mg/l
Diethyl Phthalate	no criterion	-----	-----	350 mg/l
Di-n-Butyl Phthalate	no criterion	-----	-----	34 mg/l
Phenol	no criterion	2.56 mg/l	10.2 mg/l	3.5 mg/l
2-Chlorophenol	no criterion	2.00 mg/l	4.38 mg/l	0.1 µg/l
2-Nitrophenol	no criterion	no data	2.30 mg/l	no criterion
2,4-Dichlorophenol	no criterion	0.37 mg/l	2.02 mg/l	3.09 mg/l
2,4-Dimethylphenol	no criterion	no data	2.12 mg/l	400 µg/l
1,4-Dichlorobenzene	no criterion	0.76 mg/l (4)	1.12 mg/l (4)	400 µg/l (4)
Hexachloroethane	no criterion	0.54 mg/l	0.98 mg/l	19, 1.9, & 0.19 µg/l (3)
1,1,2,2-Tetrachloroethane	no criterion	2.40 mg/l	9.32 mg/l	1.7, 0.17, & 0.017 µg/l (3)

(1) Values reported taken from EPA literature review during criteria development.

(2) No criterion indicates that the EPA could not obtain sufficient and/or appropriate data to develop meaningful criterion.

(3) Estimated risk level corresponding to an additional carcinogenic risk of 1 in 10⁵, 1 in 10⁶, and 1 in 10⁷ persons, respectively.

(4) Total of all three isomers.

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Matrix Considerations

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A secondarily treated combined petrochemical wastewater was chosen as the wastewater matrix for three main reasons: 1) petrochemical industries are known to generate wastewaters containing the toxicants of interest; 2) carbon treatment has been proposed as an effective tool for polishing secondary effluents; and 3) the results should provide some insight on the amenability of industrial effluents to carbon treatment and economic feasibility of such treatment.

The Gulf Coast Waste Disposal Authority's (GCWDA) 40-acre facility at Texas City, Texas was deemed particularly appropriate for this study, because this facility treats spent process waters generated by two local petrochemical industries. The influent to the treatment plant is composed exclusively of wastewaters from adjacent Monsanto and Union Carbide processing plants, with the exception of domestic wastes produced on site and within these two plants. The plant handles an average flow of 10-15 MGD utilizing a treatment scheme typical of extended aeration facilities. After primary sedimentation on-site at both petrochemical plants, treatment plant influent flows into an equalization basin. From arrival at the equalization basin to final effluent discharge, complete treatment requires about 16 days, with approximate retention times as follows: after one day, equalization basin effluent flows to 64750m³ limited aeration basins where intermediate sedimentation occurs during the 7 day retention period; effluent from the limited aeration basins then flows to secondary aeration basins where aeration intensity is magnified; after a 5 day retention in the secondary aeration basins, the wastewater then moves to 60700m³ secondary sedimentation basins where some degree of facultative anaerobic treatment is affected in the 3 day retention period. The effluent from secondary sedimentation basins is discharged into Engineers Ditch, which subsequently empties into Galveston Bay. A summary of plant influent and final effluent wastewater characteristics for 5-29-80, obtained from GCWDA lab personnel is presented in Table 13, along with average values and standard deviations for 28 days prior. A set of plant effluent samples were collected on 5-29-80 for use in subsequent lab-scale carbon studies.

Prior to spike addition and carbon treatment, wastewater samples were membrane filtered to reduce biological activity. Although filtration will alter conditions encountered in full-scale carbon column operation somewhat, justification is based upon the intent of the study and laboratory scale feasibility. This study was designed to evaluate the interactions of dissolved organics and competitive phenomena occurring in active carbon adsorption systems. Because carbon adsorption is a phenomenon involving dissolved components, removal of bacteria and particulate matter by filtration should not significantly influence the nature of these interactions.

Justification is also based upon feasibility of laboratory-scale column operation. The extremely high algal density of the GCWDA plant effluent, reflected in an extracted chlorophyll value of approximately 1180 mg/m³, would require column backwashing so frequently that continuous-flow operation would not be possible. Reduction of biological activity was also required because of relatively long residence times of

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TABLE 13. GCWDA TEXAS CITY, TEXAS WASTEWATER CHARACTERISTICS

Sampling Point	pH	Flow (MGD)	COD (mg/l)	TOC (mg/l)	TSS (mg/l)	VSS (mg/l)	Total N (mg/l)	Total P (mg/l)
Monsanto Influent ⁽¹⁾ Sampling Date 28 Days Prior ⁽²⁾ St. Dev. ⁽³⁾	7.2 7.5 0.7	1.85 3.00 0.99	257 215 135	49 51 71	116 91 44	67 45 23	15.4 9.4 4.0	3.5 3.7 2.4
Union Carbide Influent (Concentrated Stream) Sampling Date 28 Days Prior St. Dev.	8.1 8.0 0.1	1.56 0.91 0.38	2000 2354 214	550 660 123	28 43 11	12 24 7	40.5 40.4 4.0	48.0 52.0 7.1
Union Carbide Influent (Dilute Stream) Sampling Date 28 Days Prior St. Dev.	9.2 9.5 0.6	9.99 8.14 0.82	572 678 191	105 129 42	48 63 20	14 25 10	52.9 24.3 8.7	7.0 2.8 1.8
Plant Final Effluent Sampling Date 28 Days Prior St. Dev.	8.5 8.2 0.2	12.56 12.53 1.6	160 182 32	25 30 7.8	38 31 6.6	23 23 5.6	15.3 14.5 2.7	7.0 6.9 0.1

(1) Sampling date was 5-29-80

(2) Average values for period 28 days prior to sampling date.

(3) Standard deviation for the values 28 days prior to sampling date.

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influent in carbon column reservoirs. Reservoir residence times of up to 24 hours were required to utilize continuous-flow column systems, so removal of biological activity was necessary to prevent possible matrix alteration, and/or, utilization of spiked organics prior to carbon treatment.

Column Design And Operation

Preliminary experiments were conducted with phenol in single solute, deionized-distilled water (DIW) systems to investigate the effects of carbon mesh size, column dimensions, and carbon contact time on the adsorption mechanism. The studies were designed such that each parameter was varied individually, with other parameters held constant, in order to optimize bench-scale operation. Results from these studies indicated that adsorption efficiency and run time logistics were optimized by using the following set of parameters:

Column dimensions - 8 x 300 mm;
Carbon bed dimensions - 8 x 100 mm;
Carbon mesh size - 12 x 18;
Carbon mass - 2,000 g; and
Flow rate (EBCT) - 0.7 ml/min (7.5 min).

Virgin Calgon Filtrasorb 400, a bituminous-based active carbon, was obtained in a 22.2 kg (60 lb) bag containing 8 x 30 mesh carbon. This active carbon was used in all adsorption studies, except where otherwise noted. The carbon was sieved to obtain a 12 x 18 mesh fraction, DIW rinsed to remove fines, and dried for 24 hours at 175°C prior to use. This size fraction was selected because it is suitable for use in field scale columns, the narrower particle size range yields more uniform bed depths per given mass of carbon, and because the preliminary experiments indicated that adsorption capacity was comparable to smaller size fractions.

After weighing 2.00 g of the dried carbon in a tared beaker, the carbon was covered with approximately 200 ml of DIW and slowly agitated overnight to remove gases trapped within the pore structure. The carbon was then packed into the glass columns as a slurry, backwashed, and settled by tapping. Columns were gravity fed from overhead reservoirs, and flow rates were controlled with teflon stopcocks. Carbon columns were backwashed with distilled water at roughly one-week intervals to maintain flow rates. Approximately one-liter effluent fractions were collected daily; exact volumes were measured, and elution times recorded. For wastewater runs, column fractions were collected on ice to minimize chemical change and inhibit bacterial growth during fraction elution. All collected fractions were extracted and concentrated immediately, and extracts were stored at -10°C prior to analysis.

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Adsorption Systems

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Three basic types of adsorption systems were selected for bench scale studies: single solute DIW matrices; multiple solute DIW matrices; and, multiple solute wastewater matrices. Since no other competing species were present, single solute DIW systems were used to represent optimal adsorption conditions, and establish maximum carbon capacities. Six toxicants, representing each of the organic groups of interest, were chosen for single solute studies, and run in DIW matrices at equimolar concentrations (except for acenaphthylene). To evaluate the nature and extent of solute competition for adsorption sites, and to determine if component breakthrough in multiple component matrices could be predicted from single solute capacity data, these six solutes were combined in a multiple component DIW matrix. Each of the organics was present in the combined system at the concentration used in the single component runs. To determine the effects of further matrix complexity on adsorptive phenomena, wastewater samples were spiked with the same six organics at comparable concentration levels. All operational parameters were held constant in both DIW and wastewater experiments. Organic components used in single solute and six solute studies are given in Table 14 along with influent concentrations and aqueous solubility.

TABLE 14. SPIKE COMPONENTS USED IN SINGLE AND SIX-SOLUTE MATRICES

Component	Solubility (mg/l)	Influent (μ M)	Concentration (mg/l)
Phenol	93000	100	9.4
2,4-dimethylphenol	4700	100	12.2
Dimethyl Plthalate	4000	100	19.4
Diethyl Phthalate	1000	100	22.2
Acenaphthylene	3.9	72 ⁽²⁾	11.0 ⁽²⁾
1,4-dichlorobenzene	79	100	14.7

(1) Data is from Dobbs and Cohen, 1980.

(2) Greater solubility facilitated by use of 1% methanol/water solution.

Subsequent studies were undertaken to investigate adsorptive phenomena in DIW and wastewater matrices spiked with additional organics, and at considerably lower concentration levels. In addition to further defining competitive adsorption relationships, these experiments were used to evaluate TOC/COD breakthrough vs. specific toxicant breakthrough in the spiked wastewater runs. The initial experiments in this series involved spiking twelve compounds (listed in Table 15) into both matrices at 5 μ M each.

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TABLE 15. SPIKE COMPONENTS USED IN TWELVE-SOLUTE MATRICES

Compound	Solubility ⁽¹⁾ (mg/l)	Influent (μ M)	Concentration (mg/l)
Phenol	93000	5	0.470
2-chlorophenol	28500	5	0.643
2-nitrophenol	2100	5	0.695
2,4-dimethylphenol	4700	5	0.610
2,4-dichlorophenol	4500	5	0.815
Dimethyl Phthalate	4000	5	0.970
Diethyl Phthalate	1000	5	1.111
Di-n-butyl Phthalate	4500	5	1.390
Acenaphthylene	3.9	5	0.760
Phenanthrene	1.3	5	0.890
1,4-dichlorobenzene	79	5	0.735
Hexachloroethane	50	5	1.185

(1) Solubility data from Dobbs and Cohen, 1980.

The final set of bench scale experiments were used to address several issues in addition to those described previously. These carbon column studies employed an eleven-component spike matrix, ten of which were common to the twelve-component system, but with 1,1,2,2-tetrachloroethane added. 1,1,2,2-tetrachloroethane, a relatively low carbon affinity component, was added to the adsorption matrix to extend the range of adsorbate affinities on the low end of the spectrum. This adsorption matrix was also used to examine reproducibility of the test methodology, with duplicate runs being made in both DIW and wastewater matrices.

Finally, this adsorption matrix was used for comparison of adsorptive characteristics for two other active carbons; regenerated Calgon Filtrasorb 400, and virgin Witco 950, a petroleum-based active carbon. The regenerated Filtrasorb 400 carbon, obtained from the Calgon Corp., had come from a drinking water treatment facility, but otherwise was of unknown regeneration history. Both of these carbons were prepared for use exactly as described for the virgin Filtrasorb 400, and all column parameters were similarly identical. The eleven compounds used for these column runs are presented as Table 16 below.

Column Monitoring Strategy

Parameters of interest for evaluation of carbon performance include: volume treated to initial adsorbate breakthrough; carbon capacity at selected adsorbate breakthrough points; ultimate carbon capacity;

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TABLE 16. SPIKED COMPONENTS USED IN ELEVEN-SOLUTE MATRICES

Compound	Solubility ⁽¹⁾	Influent (μ M)	Concentration (mg/l)
Phenol	93000	5	0.470
2-chlorophenol	28500	5	0.643
2-nitrophenol	2100	5	0.695
2,4-dimethylphenol	4700	5	0.610
2,4-dichlorophenol	4500	5	0.815
Dimethyl Phthalate	4000	5	0.970
Diethyl Phthalate	1000	5	1.111
Di-n-butyl Phthalate	4500	5	1.390
Acenaphthylene	3.9	5	0.760
1,4-dichlorobenzene	79	5	0.735
1,1,2,2-tetrachloroethane	2900	5	0.839

(1) Solubility data from Dobbs and Cohen, 1980.

adsorbate elution order; carbon capacity reduction in complex matrices; and, TOC/COD breakthrough curves. Eleven- and twelve-component, low spike level wastewater runs were used to examine TOC/COD breakthrough vs. breakthrough of the specific toxicants as measured by GLC techniques. Because of concern over the sensitivity (approximately 1000 times less for TOC/COD vs. GLC) and efficiency of TOC/COD carbon column monitoring parameters, spike components were carefully selected to more accurately assess these relationships. Within each adsorption matrix, at least one of the more soluble compounds was selected from each of the four groups of organic compounds, since these compounds should exhibit the least carbon affinity and therefore breakthrough most rapidly. Thus by utilizing compounds from each class which exhibit a range of carbon affinities, results should provide a better indication of the accuracy with which TOC/COD parameters reflect the breakthrough of specific toxicants.

Several studies have shown that column monitoring techniques currently in use in the United States are poor indicators of toxicant breakthrough. A monitoring study conducted by the EPA of six field installations has shown that odor breakthrough, a commonly used monitoring parameter, occurs much later than breakthrough of general organic compounds (Robeck, 1975). The removal of odor can be successful for years, whereas the organic removal as indicated by carbon chloroform extract (CCE) or carbon alcohol extract (CAE) will occur over a period of only weeks. Similar results were obtained by Love (1973) at GAC facilities in Ohio and Massachusetts. After 33 weeks of service GAC beds at the Piqua, Ohio, plant were still producing odorless water. However, monitoring the organics in the influent and effluent by the low-flow carbon adsorption method (CAM) sampler showed that capacity for CCE was essentially exhausted after 10 weeks of operation. At Lawrence, Massachusetts, removal of CCE was found to last

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14 weeks, and the capacity for CAE lasted only nine weeks. After nine weeks the CAE in the bed effluent was greater than that in the influent, but odor removal remained effective through the ninety-first week.

Studies on haloform adsorption have shown that COD and TOC are particularly poor indicators of toxicant breakthrough for these compounds. Rook (1976) investigated the adsorption of mixtures of haloform compounds spiked into river water. Using a 12-minute carbon contact time, he found breakthrough of spiked haloforms to occur after two to twenty-two days of operation, although COD/TOC data indicated column performance was still quite good. However, a contradictory study by Robeck (1975) using pesticides as adsorbates indicated that COD/TOC determinations provide a good monitoring tool for high carbon affinity compounds such as pesticides.

In matrices where organic toxicants are of concern, analysis of specific contaminants in carbon effluents is the most reliable column monitoring technique available. These techniques also afford significant sensitivity advantages, with gas chromatography yielding sensitivities of less than $1\mu\text{g/l}$ to $10\mu\text{g/l}$, dependent upon the particular compound and analytical technique. However, such determinations are generally too elaborate and expensive for routine monitoring, so several more sophisticated alternatives have been examined. West Germany has been a leader in developing techniques more indicative of the water quality being produced at a given time and the need for carbon regeneration. Along with continued efforts at correlation of specific organics with UV absorption and fluorescence measurements the West Germans are refining microcoulometric techniques for rapid, simple detection of organochlorine compounds (Kuhn & Sontheimer, 1973). The microcoulometric technique appears to be most promising, because it enables detection of a more specific group of organic compounds, sample preparation is simple, and analytical sensitivity is excellent. Also, the organochlorine compounds are particularly appropriate for monitoring, because they are often difficult to decompose biologically and frequently hazardous to human health. However, for certain matrices this method would be of limited utility, as it is dependent upon the presence of halogenated organics. In the current investigation for example, the majority of the toxicants found in the petrochemical matrix are not halogenated species.

Sampling

Secondarily treated combined industrial wastewater used in activated carbon treatment studies was obtained from the 40-acre treatment facility of the Gulf Coast Waste Disposal Authority at Texas City, Texas. The final effluent from this facility was grab sampled from a pump station located just prior to the point of discharge (coincident with the plant's effluent monitoring station). This biologically treated effluent was subsequently pumped into the first of three 5.1 cm x 2 meter pyrex columns containing a mixed filter media of gravel, garnet, and sand. Effluent from the first mixed media column was then passed through the other two columns by gravity flow prior to collection. Mixed media filter effluent from the final filter was collected in hexane rinsed 45 liter pyrex carboys, stoppered, and packed in ice to minimize biological

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and chemical changes during transportation. Plant influents, and filtered and unfiltered final effluent samples from this facility were also collected in zero headspace four-liter glass bottles equipped with teflon lined screw caps and packed in ice. The iced samples were transported by van back to the water chemistry laboratory at The University of Texas - Dallas, and stored at 4°C until needed.

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SITE STUDIES

Two larger-scale studies were conducted on GAC treatment of unspiked GCWDA plant effluent. These studies were designed to evaluate the breakthrough characteristics of selected contaminants under adsorption conditions encountered in practical applications (significantly lower, heterogeneous concentration levels). The first of these studies was performed in the field at the GCWDA treatment facility; while the second, of longer duration, was run in the water chemistry laboratory at the University of Texas at Dallas. Because of low contaminant concentration levels in the plant effluent and relatively short column run times, two approaches were used for examination of toxicant breakthrough: 1) analysis of toxicant movement within the carbon column itself; and, 2) analysis of toxicant breakthrough in the column effluent. The toxicants selected for these studies included a number of compounds common to the bench-scale studies, and several additional compounds which had been previously confirmed to be present in the GCWDA plant effluent (see Table 17 below).

TABLE 17. TOXICANTS MONITORED IN UNSPIKED GAC STUDIES

Phenols	Phthalate Esters
Phenol	Dimethyl Phthalate
2-nitrophenol	Diethyl Phthalate
2-chlorophenol	Di-n-butyl Phthalate
2,4-dimethylphenol	
2,4-dichlorophenol	Polynuclear Aromatic Hydrocarbons
2,4,6-trichlorophenol	Acenaphthene
4,6-dinitro-o-cresol	Acenaphthylene
	Fluorene
Chlorinated Hydrocarbons	Anthracene
1,4-dichlorobenzene	Phenanthrene
	Pyrene

Results of these investigations were used for comparison with adsorption phenomena observed in bench-scale studies, and to better assess the feasibility of GAC treatment of industrial wastewaters under conditions more closely reflecting full-scale operation.

The field study was conducted in conjunction with sample collection for bench-scale studies on 5-29-80. Sand filtered GCWDA plant effluent served as the carbon column influent for this study, which was run for

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approximately 33 hours. The emphasis of this short duration field study was to evaluate the progressive movement of the toxicants of interest within the carbon column. Operational parameters used in the study were as follows:

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Column Dimensions - 7.5 cm ID x 100 cm;
Column Surface Area - 44 cm²;
Carbon Bed Dimensions - 7.5 cm x 21 cm;
Carbon Bed Volume - 928 cm³;
Carbon Mass - 425 g;
Flow Rate - 125 ml/min;
EBCT - 7.5 min.;
Study Duration - 33.4 hours; and,
Water Volume Treated - 248.5 l (268 bed volumes).

Virgin Calgon Filtrasorb 400 activated carbon was used as the adsorbent in both studies. Carbon preparation and column packing were performed exactly as described previously (see Bench-Scale Studies).

The column was operated in the downflow mode. A stainless steel screen was used at the top of the column to prevent disruption of the carbon orientation. One-liter carbon column effluent samples were collected at 10-liter intervals over the duration of the study period. Unfiltered and sand filtered GCWDA plant effluent samples were collected at the initiation and conclusion of the column run for determination of influent toxicant levels. At the conclusion of the study, the carbon column was gravity drained, sealed, and packed in ice for transport back to the laboratory. Column influent and effluent samples were similarly packed in ice, and transported by van back to the water chemistry laboratory at the University of Texas at Dallas for subsequent analysis. Upon return to the lab, the carbon column was sectioned and Soxhlet extracted for subsequent analysis.

The second investigation on GAC treatment of the unspiked industrial wastewater was performed in the laboratory. Unfiltered final effluent samples from the GCWDA treatment facility were collected on 4-21-81 in 45 liter pyrex carboys, and transported by van back to the lab. Prior to initiation of the study (less than 16 hours after sample collection) and during the column run, the wastewater samples were stored at 4°C to minimize biological and/or chemical changes in wastewater composition. Before utilization, the wastewater was pumped from the 4°C storage area to a 4 liter reservoir above the carbon column. Maintaining the water level at 2.5 liters in the reservoir resulted in a 35-minute retention time, which allowed the wastewater temperature to rise to approximately 19°C prior to introduction into the carbon column. With this continual pump design, wastewater integrity could be preserved by storage at 4°C, yet utilized at a reasonable influent temperature with minimal reservoir retention time.

The carbon column was operated in the downflow mode, with key operational parameters as follows:

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Column Dimensions - 4.7 cm x 60 cm;
Column Surface Area - 17.4 cm²;

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Carbon Bed Dimensions - 4.7 cm x 30 cm;
Carbon Bed Volume - 520 cm³;
Carbon Mass - 208 g;
Flow Rate - 70 ml/min;
EBCT - 7.5 min;
Study Duration - 84 hours; and,
Water Volume Treated - 354 l (679 bed volumes).

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A three-way stopcock was used at the bottom of the carbon column so that effluent could be diverted in one of two directions. In the first position, column effluent was diverted so as to flow through a detachable column of porous polymer adsorbent (XAD 2 & 7). The stopcock assembly was designed such that the carbon column effluent could be aspirated through the porous polymer column without adversely effecting solution flow rate through the carbon column. This technique was used as an additional method for extraction and concentration of organic contaminants in the GAC column effluent. All carbon column effluent, except for small volumes collected for other extraction procedures, was passed through porous polymer columns affecting much greater contaminant concentration factors than feasible with liquid-liquid extraction techniques. Porous polymer adsorbent columns were changed at 20- to 55-liter intervals, at which time the stopcock was rotated to the second position and one-liter carbon effluent samples were collected for subsequent liquid-liquid extraction. The carbon column flow rate was checked on each one-liter sample collected, and found to vary less than 1% over the entire column run. All effluent and porous polymer samples were extracted immediately after collection, and concentrates were stored at -10°C until analysis. Carbon column influent samples were also liquid-liquid extracted for determination of concentration levels for each toxicant of interest. Upon completion of the adsorption study, the carbon column was drained, sectioned, and Soxhlet extracted for analysis of toxicant breakthrough zones.

Results from both porous polymer extractions and carbon extractions are semi-quantitative, in that these values are not corrected for extraction efficiency. No attempt was made to approximate compound recoveries for these procedures because of the complexity of the systems, and the purpose of these analyses. Both procedures were used to examine relative breakthrough relationships and trends in the carbon columns, and so did not require the use of absolute concentration values.

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SECTION 6

ANALYTICAL METHODS

BENCH STUDIES

Analysis of wastewater samples and spiked carbon column effluents for specific organic constituents generally involved extraction of the organics from the water matrix, extract concentration, column chromatographic cleanup procedures to minimize interference, and quantification of individual components by gas-liquid chromatography (GLC). Of the various methods available for extraction, concentration, and analysis of organics from water and wastewater matrices, porous polymer resins and liquid-liquid techniques were selected for further evaluation. Spike recovery and reproducibility of these methods were evaluated to determine the best method for use in subsequent carbon column studies. Liquid-liquid extraction was selected for all analyses involving semi-volatile organic components in both distilled-deionized water (DIW) and wastewater matrices. Semi-volatile organics include all spike components except for 1,1,2,2-tetrachloroethane.

Separatory funnel liquid-liquid extraction techniques as described in the USEPA "Guidelines for the Analysis of Pollutants" (Federal Register, 12-3-79) were used for extraction of organic solutes in all single component carbon column studies. Column effluent fractions (600- to 1000-ml volumes) were serially extracted with three 50-ml aliquots of dichloromethane, and the combined extracts were dried over anhydrous sodium sulfate to remove residual water. Dried extracts were collected in Kuderna-Danish evaporative flasks fitted with 4-ml graduated receivers, and concentrated to approximately 2 ml. Kuderna-Danish flasks were then removed, and receivers were placed under a gentle stream of nitrogen gas to further concentrate extracts to ≤ 1.0 ml.

In all wastewater and multiple component DIW column studies, a continuous liquid-liquid extractor was employed in place of the separatory funnel technique. Selection of the continuous extractor for these studies was based on preliminary data which indicated that several distinct advantages could be realized. Significant advantages include: better reproducibility; higher spike recoveries; lower loss of the more volatile components; and, elimination of emulsion problems encountered with separatory funnel procedures. Using the Soxhlet principle with dichloromethane as the solvent, the continuous extractors were allowed to

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repeatedly extract sample solutions over a 20 hour period, yielding recovery efficiencies of 45-95%. Extracts were immediately concentrated to a final volume of less than 1.0 ml as described above. Extracts were subsequently diluted to 1.0 ml (as measured by syringe) prior to internal standard addition and chromatographic analysis.

Gas-liquid chromatography was used for the analysis of specific organic components in all carbon column studies, with the internal standard method selected for peak quantification. In single, six-, and twelve-component matrices chromatographic analyses were performed on a Varian 2100 chromatograph equipped with flame ionization detection (FID) and coupled to a Perkin-Elmer Sigma 10 electronic integrator. Phthalate esters, phenols, and PNA's were run on a 2mx2mm I.D. glass column packed with 1% SP-1240DA on 100/120 mesh Suplecoport. Gas chromatographic conditions were as follows: injection temperature 225°C; detector temperature 250°C; oven temperature 60°C to 150°C at 6°C/minute with a 2 minute initial hold; and, carrier gas (N₂) 25ml/minute at 60 PSI. Twenty microliters of a concentrated solution of 2,3,5-trimethylphenol internal standard was added to each 1.0ml extract prior to chromatographic analysis.

A 2mx2mm I.D. glass column packed with 1.5% SP2250/1.95% SP-2401 on 100/120 mesh Supelcoport was used for 1,4-dichlorobenzene analysis, with 1,2-dichlorobenzene as the internal standard for quantification. Gas chromatograph (GC) operating conditions were exactly as described above, except that the column oven was operated at 60°C isothermally. FID detection limits for each compound from water extracts, corrected for extraction efficiency, are presented in Table 18.

TABLE 18. COMPONENT DETECTION LIMITS FROM WATER MATRICES

Compound	FID Detection Limit (µg/l) ⁽¹⁾	
	Single Component Matrix	Six- and Twelve-Component Matrix ⁽²⁾
Phenol	6	7
2,4-dimethylphenol	3	3
Dimethyl Phthalate	5	5
Diethyl Phthalate	5	5
1,4-dichlorobenzene	4	4
Acenaphthylene	4	5
Phenanthrene	-	5
Hexachloroethane	-	4
2-chlorophenol	-	5
2-nitrophenol	-	6
2,4-dichlorophenol	-	6
Di-n-butyl Phthalate	-	5

(1) Detection limits for packed columns, based on values corrected for extraction efficiency.

(2) Detection limits approximately equal in both DIW and wastewater matrices.

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In eleven-component DIW and wastewater column runs, capillary GLC techniques were employed for component separation and quantification. In these studies the increased sensitivity and resolution afforded by capillary column technology was utilized to overcome problems previously encountered in the twelve-component studies where relatively low spike concentrations were used. This problem was particularly apparent in the wastewater matrix where background interference was often significant. A 7.5mx0.25mm I. D. fused silica capillary column coated with SE-54 (94% methyl silicone, 5% phenyl silicone, and 1% vinyl silicone) was used for separation and quantification of all semi-volatile components in these runs. Analyses were performed on a Hewlett-Packard (HP) 5840 gas chromatograph equipped with flame ionization detectors and a Hewlett-Packard 5840A electronic integrator for peak area quantification. The chromatograph was operated in the splitless injection mode, with a 0.25 minute injection time for 0.5µl injection volumes, and a 30ml/minute injector purge rate upon completion of the 0.25 minute injection period. Gas chromatographic conditions were as follows: capillary injector temperature 235°C; FID temperature 275°C; oven temperature 40°C to 200°C at 6°/minute with a 4-minute initial hold at 40°C; carrier gas (He) flow 25cm/second at 4 PSI; and, FID make-up gas (He) flow 30ml/minute. FID detection limits for each compound from water extracts, corrected for extraction efficiency, are listed in Table 19.

In the eleven-component DIW adsorption matrix, 1,1,2,2-tetra-chloroethane was analyzed by a modified version of the liquid-liquid extraction procedure described by Henderson et al. (1976). Carbon

TABLE 19. COMPONENT DETECTION LIMITS FROM WATER MATRICES

Compound	FID Detection Limit ⁽¹⁾	
	DIW Matrix	Wastewater Matrix
Phenol	0.4	0.5
2-chlorophenol	0.3	0.5
2-nitrophenol	0.8	0.9
2,4-dimethylphenol	0.4	0.5
2,4-dichlorophenol	0.4	0.8
Dimethyl Phthalate	0.3	0.4
Diethyl Phthalate	0.4	0.9
Di-n-butyl Phthalate	0.8	0.9
1,4-dichlorobenzene	0.9	0.9
Acenaphthylene	0.7	0.9

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(1) Detection limits for SE-54 capillary column, based on values corrected for extraction efficiency.

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column effluent samples were collected in 20ml vials fitted with teflon-lined septa caps, and sealed such that all headspace was excluded. These samples were then stored at 4°C until analysis. Prior to analysis, a 3.0ml aliquot of the aqueous solution was removed with a syringe through the septa and replaced with 1.0 ml of n-hexane. Sample vials were then vigorously hand shaken for 2 minutes, and a 0.5ml portion of the n-hexane extract was removed for addition of the 1,1,1-trichloroethane internal standard. These extracts were analyzed for 1,1,2,2-tetrachloroethane using a Hewlett-Packard 5840 gas chromatograph equipped with a ⁶³Ni electron capture detector (ECD) and interfaced to a HP-5840A electronic integrator. A 2mx2mm I.D. glass column packed with 12.5% squalane on 60/80 mesh acid-washed chromosorb W was used for separation of volatile components. Gas chromatograph operating conditions were as follow: injection temperature 225°C; detector temperature 300°C; oven temperature 65°C isothermal; and, carrier gas (He) flow 40 ml/minute at 60 PSI. Using a 3µl injection volume with the solvent flush injection technique, the DIW water extract detection limit, corrected for extraction efficiency, was 0.8µg/l for 1,1,2,2-tetrachloroethane.

Volatile halogenated organics in the wastewater adsorption matrix were analyzed by a modified version of the purge and trap technique described by Bellar and Lichtenberg (1974). The purge and trap technique was used in conjunction with selective detection for this system to decrease potential interferences from the complex matrix, and to increase detection sensitivity. Column effluent samples were collected in 6.0ml pyrex vials fitted with teflon-lined speta caps, sealed with zero headspace, and stored at 4°C prior to analysis. Five ml aliquots of each sample were withdrawn by syringe and injected into the purge vessel for concentration. A 21cmx2mm I.D. stainless steel tube packed with equal lengths of Davidson Grade 15 silica gel, followed by 60/80 mesh Tenax GC, and finally by 60/80 mesh coconut activated charcoal was used as the adsorbent for trapping the purged organics. A Valco Trace Organics Concentrator purge and trap apparatus interfaced to a Tracor 560 gas chromatograph fitted with a Hall Electrolytic Conductivity Detector was used for these analyses. The 5ml water samples were purged for 11 minutes with He at 20ml/minute onto the trap, and subsequently backflushed onto a 45°C GC column by trap desorption at 180°C for 4 minutes. Following the desorption cycle, the trap material was baked at 250°C for 15 minutes, while venting the trap flow, to remove residual organics prior to the next analysis. A 2.6mx2mm I.D. stainless steel column packed with 1% SP-1000 on 60/80 mesh Carboxpack B was used for separation of the organics. Gas chromatograph conditions for these analyses were as follows: injector temperature 175°C; detector temperature 250°C; oven temperature 45°C to 220°C at 8°C/minute with a 3 minute initial hold at 45°C and a 20 minute final hold at 220°C; and, carrier gas (He) flow 30ml/minute at 60 PSI. Samples were analyzed against calibration standards prepared by spiking DIW samples with a methanol solution containing a known amount of the organics of interest. The detection limit for 1,1,2,2-tetrachloroethane was determined to be 0.4µg/l with this method of analysis.

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Selected extracts from wastewater matrix column effluents and unspiked wastewater samples were analyzed by gas chromatography/mass spectroscopy (GC/MS) for elucidation of wastewater composition, and

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verification of qualitative results from gas chromatographic analyses. Mass spectrometric identifications were performed on a Hewlett-Packard 5985 GC/MS system, utilizing a HP-5840 GC. Separation was accomplished with a 7.5m x 0.25mm I.D. SE-54 fused silica capillary column operated under the conditions described for semi-volatiles analysis in the eleven component matrix. The mass spectrometer (MS) was operated in the electron impact ionization mode at a potential of 70eV, with other MS parameters as follows: scan range - 40amu to 400amu; scan rate - 1 scan/1.3 sec; and, source temperature - 200°C.

Chemical oxygen demand and total organic carbon were determined on each fraction collected from active carbon columns treating spiked wastewater influent. COD analyses were performed by potassium dichromate digestion as outlined in Standard Methods (APHA, 1976) and by ultraviolet spectrophotometric correlation at 240nm as described by Dobbs et al. (1972). The spectrophotometric correlation procedure involved preparation of a series of dilutions of the spiked wastewater influent and using these dilutions to develop a standard curve for UV absorbance at 240nm with a 1 cm light path length. Dilutions were assigned COD values based on the value obtained for the undiluted wastewater from potassium dichromate digestions. A Varian Cary 219 ultraviolet-visible scanning spectrophotometer was used for these determinations. A COD detection limit of 3mg/l was determined for the digestion procedure, while linear results were obtained to 1mg/l COD with the spectrophotometric correlation methodology. TOC analyses using non-dispersive infrared detection were performed on an Oceanography International Model 0542B organic carbon analyzer, in accordance with the procedure outlined in Standard Methods (APHA, 1976). Samples were acidified to a pH < 1 at the time of collection to drive off inorganic carbon prior to TOC analyses. Utilizing 50µl injection volumes and the direct injection module, a detection limit of 0.5mg/l TOC was established. Quantification was relative to a standard curve generated by injecting a series of known concentrations of potassium acid phthalate, which proved linear over the range of 0.5-50.0 mg/l TOC.

SITE STUDIES

Liquid-liquid extractions were performed with continuous extraction apparatus in both site studies. Sample extractions were performed exactly as described in the bench scale studies, except that each sample was extracted at both acidic and basic pH. Samples were adjusted to pH=12 with concentrated sodium hydroxide prior to the initial extraction so that sample extracts contained predominately base/neutral organic species. The sample pH was subsequently adjusted to pH 1 with concentrated nitric acid, and reextracted to remove the acidic (dissociable) species. Both acidic and basic extracts were concentrated to a final volume of 1.0 ml by the procedure described previously (see Bench Studies).

FID detection limit for water extracts were found to be the same as those observed in bench studies for common compounds (see Table 19). FID detection limit for other compounds of interest in site studies are given

in Table 20 below.

TABLE 20. DETECTION LIMIT FOR COMPOUNDS UNIQUE TO SITE STUDIES

Compound	FID Detection Limit ⁽¹⁾ (µg/l)
2,4,6-trichlorophenol	0.8
4,6-dinitro-o-cresol	1.6
Anthracene	1.0
Phenanthrene	1.0
Acenaphthene	0.9
Fluorene	0.8
Pyrene	1.2

(1) Detection limits for 30 m SE-54 capillary column, based on values corrected for recovery efficiency from the wastewater matrix.

The porous polymer adsorbent columns used for sample extraction in the laboratory study consisted of two layers of XAD resins. The columns (0.8 cm ID x 20 cm) contained a 6 cm upper layer of XAD-2, followed by a 6 cm layer of XAD-7 beneath. XAD-7 was used in conjunction with XAD-2 because of its superior affinity for phenolic compounds. The XAD columns were blown dry after use, and attached to 300 ml reservoirs containing diethyl ether. The XAD columns were then eluted by gravity flow with 100 ml of diethyl ether to remove the organics from the resin. Resin extracts were dried over anhydrous sodium sulfate, and concentrated to 1.0 ml as previously described.

Soxhlet extraction apparatus was used in both studies for extraction of organic contaminants from activated carbon samples. The carbon was removed from the columns by inserting a plunger of column diameter and slowly pushing out the appropriate length of carbon. The carbon was collected in pyrex beakers and then transferred to pyrex extraction thimbles. In the field study the column was sectioned in unequal lengths, from shortest at the top (influent end) to longest at the effluent end. The entire carbon mass of the upper four sections was extracted, while subsamples of the larger bottom three sections were used for extraction. Representative subsamples of the bottom three sections were obtained by placing the entire mass of each in separate beakers, and slowly agitating the carbon with a glass rod. After 10-15 minutes of agitation, the samples were assumed to be homogeneous and subsamples were collected for extraction. In the laboratory study the column was sectioned in six equal lengths, and the entire carbon mass of each section was extracted.

The carbon samples were extracted with 250 ml of a 1:1 (V/V) acetone:hexane solution for a 24-hour period. Extracts were dried over anhydrous sodium sulfate and concentrated to a final volume of 10.0 ml with Kuderna-Danish flasks. After extraction, the carbon was removed from the extraction thimble, placed in a tared beaker, and dried overnight at 105°C. Beakers were then cooled to room temperature in a desiccator and reweighed to determine the weight of carbon extracted.

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A 30 m x 0.25 mm ID fused silica capillary column coated with SE-54 was used for GLC analysis of all samples collected from site studies. The longer column was used to affect better separation than could be achieved with the 7.5 m column employed in previous studies. The internal standard method was selected for peak area quantification, using 1,2-dichlorobenzene as the internal standard component. GLC analyses were performed on a Hewlett-Packard 5840 gas chromatograph equipped with flame ionization detectors and a Hewlett-Packard 5840A electronic integrator. The chromatograph was operated in the splitless mode, with a 0.25 minute injection time for 0.5 μ l injection volumes, and a 30 ml/minute injector purge rate upon completion of the 0.25 minute injection period. Chromatograph operating conditions were as follows: capillary injector temperature 235 $^{\circ}$ C; FID temperature 275 $^{\circ}$ C; oven temperature 40 $^{\circ}$ C to 210 $^{\circ}$ C with a 3 minute initial hold at 40 $^{\circ}$ C and a 10 minute final hold at 210 $^{\circ}$ C; carrier gas (He) flow 25 cm/second at 15 PSI; and, FID make-up gas (He) flow 30ml/minute.

QUALITY CONTROL

Gas chromatographic quantification of specific organic constituents was based on data generated from analyses of standard solutions prepared from analytical grade reagents and glass-distilled solvents, using the internal standard quantification method. GC analysis variance was estimated for each compound in the primary analytical standard using the SE-54 capillary column with 1,2-dichlorobenzene as the internal standard. Results of these analyses are summarized in Table 21, and a typical chromatogram is shown in Figure 2. Detection limit, established for each component in each adsorption system (see Tables 18-20) was defined as that concentration which produced a signal of greater than three times the baseline noise level. Standards bracketing the concentration range of interest were run to assess linearity, and to insure that sample quantification remained within the linear range of the detector employed. When necessary, sample volumes were adjusted to maintain component concentrations within this range. Because of a significant potential for instrument response to change with time, a standard was injected periodically to verify instrument response and method calibration. Integrator calibration was based on at least three injections of the standard solution, and if instrument response fell outside of the range of deviations established initially (see Table 21) the instrument was recalibrated.

In order to assure more accurate sample quantification and to assess overall procedural variation, replicate DIW and wastewater aliquots were spiked to determine approximate recovery efficiency for each component of interest. Extraction efficiencies were determined by assessing spike recovery within the matrix employed for each carbon column test, and over a concentration range from that of near detection to influent levels. To better approximate recoveries for column studies involving wastewater matrices, determinations were made by spiking effluent from a carbon column treating unspiked wastewater. Effluent fractions from this carbon column blank were spiked to evaluate the effect of increasing matrix complexity on spike recovery. When required, a similar procedure was used to determine

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TABLE 21. ANALYTICAL VARIANCES FOR EACH COMPONENT OF THE CALIBRATION STANDARD⁽¹⁾

Compound	RT ⁽²⁾	Actual ⁽³⁾ Conc. (mg/l)	Average ⁽⁴⁾ Analyzed Conc. (mg/l)	Standard Devia- ⁽⁴⁾ tion Analyzed Conc. (mg/l)
Phenol	5.65	24.2	25.1	1.6
2-chlorophenol	5.42	23.8	24.3	0.9
2-nitrophenol	9.41	77.7	81.7	3.9
2,4-dichlorophenol	10.38	30.0	29.0	2.7
2,4-dimethylphenol	10.18	28.4	29.4	2.9
Dimethyl Phthalate	17.23	32.0	32.4	1.1
Diethyl Phthalate	20.10	28.6	28.0	2.3
Di-n-butyl Phthalate	26.62	34.0	32.9	1.8
1,4-Dichlorobenzene	6.01	25.6	25.2	0.6
Acenaphthylene	16.70	28.2	27.7	0.9
1,1,2,2-Tetrachloroethane ⁽⁵⁾	---	0.05	0.052	0.003
1,2-dichlorobenzene (IS)	6.63	--	---	---

- (1) Obtained by repetitive injections of the calibration standard after the GC is initially calibrated.
 (2) RT = retention time in minutes (see Figure 2).
 (3) Actual concentration equals the concentration calculated from the mass of each solute dissolved in the appropriate volume of solvent.
 (4) Mean and standard deviation values based on n=12.
 (5) Values determined by the purge and trap technique described previously.

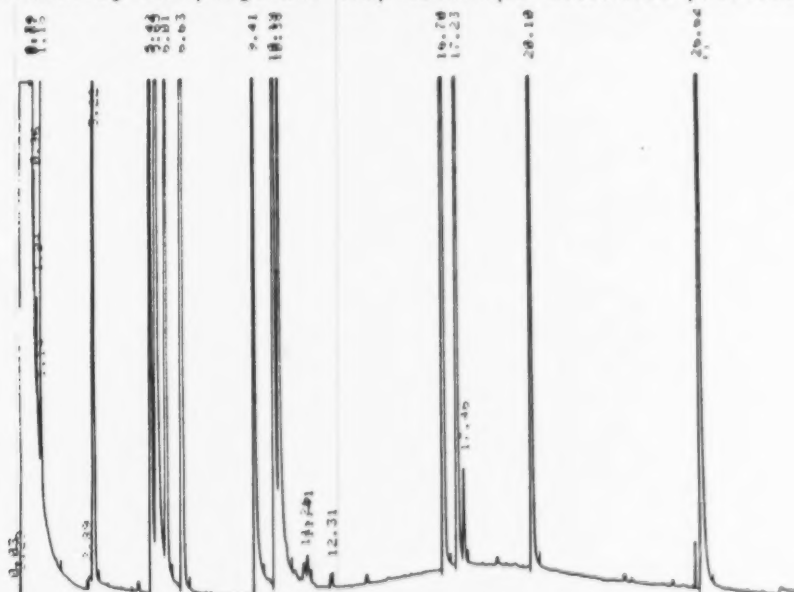


FIGURE 2. CHROMATOGRAM OF SPIKE COMPOUNDS USED IN ELEVEN-COMPONENT MATRICES.

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recovery efficiencies for samples subjected to column chromatographic clean-up procedures. Efficiencies were based upon three or more replicate extractions at each concentration, and upon at least three concentrations for each test system. These concentrations include: a low level, near the detection limit; a high level, at influent concentration; and one or more intermediate levels.

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Sample contamination was monitored carefully throughout the course of the study. All sampling apparatus, apparatus associated with the carbon columns, extraction apparatus, and concentration apparatus were constructed entirely of pyrex glass, teflon, and/or 316 stainless steel to minimize leaching and/or adsorption of sample components. All glassware, with the exception of 45-liter carboys, was heated to 525°C for one hour prior to use, and all teflon or stainless steel components were solvent rinsed and dried at 175°C. All solvents were concentrated two times greater than used in sample preparation and analyzed by GLC each time a new solvent lot was used to insure that solvent concentration produced no interfering peaks. Similarly, the DIW used in this study (produced by passing reverse osmosis treated water through a Millipore purification system) was concentrated and analyzed to assure interference-free quantification. Quality control procedures generally followed those outlined by the EPA in the "Guidelines for the Analysis of Pollutants" (Fed. Register, 12-3-79).

Carbon column effluent fractions were extracted and concentrated immediately, and concentrated extracts were stored at -10°C until GLC analysis. Samples for volatile organics were collected two carbon bed volumes after addition of fresh influent to column reservoirs, and were collected directly into zero headspace vials. Separate subsamples were withdrawn from all wastewater column effluent fractions collected and placed in glass vials for COD and TOC analyses. COD, TOC, and volatile organics samples were stored at 4°C prior to analysis.

Wastewater samples were monitored for chemical integrity over the duration of the storage period. Immediately upon return to the laboratory from the sampling site, subsamples were processed for determination of each parameter of interest. Unfiltered and sand filtered final effluent samples were liquid-liquid extracted and analyzed for changes in component concentration due to the filtration process. TOC, COD, and volatile organics analyses (VOA) were also made on the unfiltered and sand filtered samples. Each of the sample carboys was then membrane filtered as rapidly as possible to further protect against biologically mediated chemical changes. Analyses for all parameters of interest were then performed on aliquots from each carboy of wastewater collected to assess uniformity, and values obtained from these analyses were used to establish background levels for each parameter. These background levels were used to adjust the spike concentration for each component.

After initial determinations were made, the filtered wastewater was appropriately spiked in clean 45-liter carboys. Aliquots of the spiked wastewater were removed for analysis, and the remainder was decanted into zero headspace four-liter glass bottles fitted with teflon-lined screw caps. These bottles were then marked to indicate the carboy from which they originated, and stored at 4°C in the dark until needed. The aliquots of spiked wastewater removed prior to transfer were immediately analyzed for all parameters, and these levels were used as baseline values to assess chemical integrity over the storage period. Initial values for these

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parameters were also used for comparison of uniformity between spiked carboys when water from more than one was required for a column study. Representative samples from each carboy were periodically monitored for TOC and COD. Analyses for spike components were performed upon completion of each carbon column run. In studies where duplicate wastewater columns were run, each column received influent from the same carboy. Where two carboys were required to complete duplicate runs, both columns received influent from one carboy until depleted, and then from the next to maximize influent consistency.

DIW adsorption matrices were prepared by addition of concentrated solutions of spike components contained in water miscible solvents. Spiking solutions were prepared such that a minimal volume of the miscible solvent was added to one liter of DIW, and solvents were selected which had been shown to exhibit minimal affinity for the activated carbon. To reduce influent variation, DIW spiking solutions were prepared in sufficient volume to supply the influent requirements of the entire column run; spiking solutions were stored at 4°C until needed.

The analytical quality control procedures described above were also applied to the site studies. GC analytical variances for compounds unique to site studies are presented in Table 22 below. In addition to the procedures detailed above, XAD and activated carbon blanks were also processed. XAD columns were ether extracted, with the extracts being concentrated and analyzed by GLC to assure that resins had been adequately cleaned prior to use. Similarly, virgin Calgon Filtrasorb 400 active carbon blanks were Soxhlet extracted, and extracts were concentrated and analyzed by GC to insure that no previously adsorbed contaminants were present.

TABLE 22. ANALYTICAL VARIANCES FOR COMPOUNDS UNIQUE TO SITE STUDIES⁽¹⁾

Compound	Actual ⁽²⁾ Conc.(mg/l)	Average ⁽³⁾ Analyzed Conc.(mg/l)	Standard Devia- ⁽³⁾ tion Analyzed Conc.(mg/l)
2,4,6-trichlorophenol	26.3	25.5	1.9
4,6-dinitro-o-cresol	51.7	55.7	4.6
Anthracene	32.3	31.5	1.4
Phenanthrene	31.1	32.3	1.1
Acenaphthene	27.9	27.6	0.9
Fluorene	29.1	28.7	1.3
Pyrene	35.5	33.2	3.1

(1) Obtained by repetitive injections of the calibration standard after the GC was initially calibrated.

(2) Actual concentration equals the concentration calculated from the mass of each solute dissolved in the appropriate volume of solvent.

(3) Mean and standard deviation values based on n=12.

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RESULTS

PRELIMINARY STUDIES

Initial experiments were designed to optimize operational parameters for bench scale studies, to evaluate the effects of influent concentration on GAC adsorption capacity in continuous-flow systems, and to determine approximate recoveries for extraction of study compounds from water matrices. Single solute DIW matrices utilizing phenol as the adsorbate were used for investigation of concentration/capacity effects and for optimization of operational conditions. Operational parameters considered included: column dimensions; carbon particle size; and, solution flow rate or carbon contact time. Parameters were varied individually, and because of similarities in breakthrough curves, adsorptive capacity was chosen as the criterion for evaluation of carbon performance. Results from these studies, presented in Table 23, were used in selection of operational parameters described previously.

TABLE 23. EFFECT OF OPERATIONAL PARAMETERS ON CARBON PERFORMANCE

Carbon Bed Dimensions (mm)	Carbon Mesh Size	EBCT (min.)	Carbon Capacity ⁽¹⁾ (mg Adsorbed/g Carbon)
8 x 100	12/18	7.5	272
8 x 100	18/35	7.5	209
8 x 100	40/60	7.5	258
8 x 100	12/18	7.5	272
8 x 200	12/18	7.5	293
8 x 300	12/18	7.5	294
19 x 100	12/18	7.5	289
19 x 100	18/35	5.5	185
19 x 100	18/35	7.0	229
19 x 100	18/35	13.0	223

(1) Capacity values for 3000 mg/l influent concentration.

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Results from the influent concentration-carbon capacity study, presented in Figure 3, reveal a log-log linear relationship. The increase in capacity with increasing influent concentration is consistent with results obtained by Weber and Keinath (1967).

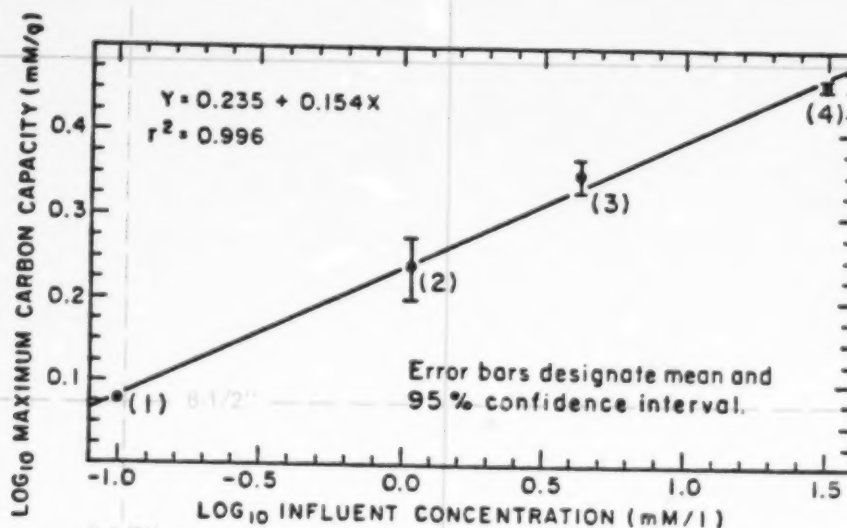


Figure 3. The dependence of maximum carbon capacity for phenol on influent column concentration.

Liquid-liquid extraction efficiencies were estimated for each of the spike compounds to allow accurate pollutant quantification. Replicate determinations were made over a range of initial concentrations for each component, and in both DIW and wastewater matrices. A range of initial water concentrations was used to evaluate the influence of concentration on the extraction process. A concentration range similar to that expected in carbon column effluents was selected for these studies. For the wastewater matrix, recoveries were determined on wastewater subjected to GAC treatment and subsequently spiked with study compounds at appropriate levels. This method was selected to more accurately reflect the influence of matrix complexity on the extraction process.

Where water concentration significantly influenced recovery, best fit curves were used to interpolate recovery values between data points. In correcting sample concentrations for extraction efficiency, the value applied was that obtained (or interpolated) for a solution of equal initial concentration. When sample concentrations fell below the lowest concentration used in recovery studies, the recovery value for the lowest concentration was applied; the same approach was used for samples exceeding the highest concentration value studied. These methods were used for correction of sample concentrations in all carbon studies. Results of the extraction efficiency studies are presented in Tables 24 and 25. Recovery values obtained from these investigations were consistent with literature data for DIW sample extractions at comparable concentration levels (Budde and Eichelberger, 1979).

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TABLE 24. STUDY COMPOUND EXTRACTION EFFICIENCIES FROM DIW MATRIX

Compound	0.1 μ M		SD(2)		Extraction Efficiency (%) (1)		5.0 μ M	
		SD		SD		SD		SD
Phenol	40.3	3.1	47.9	5.9	61.0	1.7	68.1	4.2
2-nitrophenol	84.1	3.7	86.2	4.4	95.9	7.1	102.7	6.5
2-chlorophenol	60.6	1.4	66.3	0.4	81.3	3.5	90.4	4.0
2,4-dimethylphenol	54.7	2.4	58.8	6.8	79.0	0	83.0	2.0
2,4-dichlorophenol	53.1	2.7	57.0	1.8	69.6	0.4	86.0	4.1
Dimethyl Phthalate	62.4	2.6	66.6	0.5	80.6	0.4	92.4	3.5
Diethyl Phthalate	66.2	3.4	65.0	2.2	73.3	0.6	94.0	3.1
Di-n-butyl Phthalate	45.6	2.7	48.3	1.0	56.0	2.5	94.5	3.5
Acenaphthylene	50.6	4.2	53.7	3.3	73.0	0.4	89.5	3.8
Phenanthrene	70.5	2.5	77.6	2.7	82.2	1.1	93.1	4.7
1,4-dichlorobenzene	56.1	3.1	57.6	5.6	74.0	5.1	76.2	2.8
Hexachloroethane	50.2	2.4	61.1	3.2	67.3	0.8	80.4	1.7
1,1,2,2-tetrachloroethane	61.4	3.3	65.6	2.7	71.6	2.5	79.7	3.1

{1} Extraction efficiencies at indicated initial water concentrations.
{2} SD = standard deviation expressed as % for n=3.

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TABLE 25. STUDY COMPOUND EXTRACTION EFFICIENCIES FROM THE WASTEWATER MATRIX

Compound	Extraction Efficiency (%) ⁽¹⁾					
	0.1 μ M	SD ⁽²⁾	0.5 μ M	SD	2.5 μ M	SD
Phenol	46.8	1.0	48.1	0.9	63.1	4.2
2-nitrophenol	82.4	4.1	85.9	6.1	97.1	5.4
2-chlorophenol	73.2	0.8	74.5	1.7	77.0	2.4
2,4-dimethylphenol	60.2	3.9	62.1	3.6	64.8	2.8
2,4-dichlorophenol	68.2	2.1	69.8	5.3	77.4	4.6
Dimethyl Phthalate	63.5	4.3	70.2	1.3	76.3	2.7
Diethyl Phthalate	68.7	3.6	72.3	2.4	81.1	1.6
Di-n-butyl Phthalate	50.7	5.1	60.7	4.7	67.2	3.9
Acenaphthylene	58.1	4.2	61.9	1.9	66.4	3.2
Phenanthrene	66.3	3.2	77.1	3.6	81.6	2.9
1,4-dichlorobenzene	36.3	2.8	39.7	3.3	60.9	1.4
Hexachloroethane	48.7	1.9	57.3	2.6	68.4	2.1
2,4,6-trichlorophenol	78.8	3.1	87.7	4.2	----	----
4,6-dinitro-o-cresol	18.7	6.9	36.7	7.5	----	----
Acenaphthene	72.5	2.8	80.4	3.6	----	----
Fluorene	86.6	4.5	84.4	5.2	----	----
Anthracene	64.8	4.1	73.3	3.5	----	----
Pyrene	88.4	3.6	92.1	4.4	----	----

(1) Extraction efficiencies at indicated initial water concentrations.
 (2) SD = standard deviation expressed as % for n = 3.

WASTEWATER MATRIX CHARACTERIZATION

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Final effluent samples from the 40 Acre Facility of the GCWDA were collected on two occasions for use in the bench-scale carbon column studies. On the first sampling trip, 8-11-79, a volume of plant effluent sufficient to run both six- and twelve-component spike studies was obtained. Each of these column runs required less than one carboy of wastewater, so analysis of replicate carboys to establish influent consistency was not required. Data on the background level of each parameter of interest in the membrane filtered wastewater is presented in Table 26. Table 27 summarizes the effect of the various filtration processes on the level of each parameter in the unspiked wastewater used for the twelve-component spike study. Data used to evaluate the integrity of the spiked wastewater over the duration of the storage period is summarized in Table 28.

TABLE 26. SPIKE COMPONENT BACKGROUND LEVELS FOR 8-11-79 WASTEWATER SAMPLES⁽¹⁾

Component	Conc. Carboy 1 (μg/l) ⁽²⁾	Conc. Carboy 2 (μg/l) ⁽³⁾
Phenol	0.8 ± 0.4 ⁽⁴⁾	0.8 ± 0.5
2-nitrophenol ⁽⁵⁾	0.9 ± 0.3	1.0 ± 0.3
2-chlorophenol ⁽⁵⁾	<1.0	<1.0
2,4-dimethylphenol ⁽⁵⁾	1.2 ± 0.7	1.5 ± 0.4
2,4-dichlorophenol ⁽⁵⁾	11.0 ± 1.5	10.2 ± 0.8
Dimethyl Phthalate ⁽⁵⁾	19.0 ± 2.4	16.8 ± 3.1
Diethyl Phthalate ⁽⁵⁾	26.0 ± 1.5	28.1 ± 2.2
Di-n-butyl Phthalate ⁽⁵⁾	3.8 ± 0.7	4.4 ± 1.0
Acenaphthylene ⁽⁵⁾	7.5 ± 1.3	7.7 ± 0.8
Benanthrene ⁽⁵⁾	6.1 ± 2.2	5.4 ± 2.4
1,4-dichlorobenzene ⁽⁵⁾	2.3 ± 0.6	2.4 ± 1.1
Hexachloroethane	<1.0	<1.0
COD ⁽⁶⁾	122 ± 7	125 ± 5
TOC ⁽⁶⁾	27.3 ± 1.7	26.6 ± 1.0

- (1) Values for membrane filtered wastewater samples.
- (2) Carboy 1 was used for six-solute column study.
- (3) Carboy 2 was used for twelve-solute column study.
- (4) Values are means ± 1 standard deviation for n = 3.
- (5) Presence verified by mass spectrometry.
- (6) Concentrations in mg/l.

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TABLE 27. EFFECTS OF FILTRATION ON UNSPIKED WASTEWATER (8-11-79 SAMPLING)

Component	Unfiltered	Concentration ($\mu\text{g/l}$)	
		Sand Filtered	Membrane Filtered
Phenol	$0.7 \pm 0.4^{(1)}$	0.9 ± 0.4	0.8 ± 0.5
2-nitrophenol	1.3 ± 0.6	1.2 ± 0.7	1.0 ± 0.3
2-chlorophenol	<1.0	<1.0	<1.0
2,4-dimethylphenol	2.2 ± 0.6	2.0 ± 0.7	1.5 ± 0.4
2,4-dichlorophenol	11.4 ± 0.3	10.6 ± 0.7	10.2 ± 0.8
Dimethyl Phthalate	18.7 ± 2.2	19.1 ± 2.5	16.8 ± 3.1
Diethyl Phthalate	24.4 ± 3.1	26.6 ± 2.1	28.1 ± 2.2
Di-n-butyl Phthalate	7.1 ± 3.1	5.5 ± 2.1	4.4 ± 1.0
Acenaphthylene	9.2 ± 1.7	8.4 ± 1.6	7.7 ± 0.8
Phenanthrene	5.5 ± 1.6	5.0 ± 2.0	5.4 ± 2.4
1,4-dichlorobenzene	2.2 ± 1.4	2.4 ± 1.2	2.4 ± 1.1
Hexachloroethane	<1.0	<1.0	<1.0
COD ⁽²⁾	154 ± 4	128 ± 2	125 ± 5
TOC ⁽²⁾	27.7 ± 1.3	27.3 ± 0.7	26.6 ± 1.0

(1) Values are means $\pm$ 1 standard deviation for n=3.
 (2) Concentrations in mg/l.

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TABLE 28. STORAGE EFFECTS ON SPIKED WASTEWATER (8-11-79 SAMPLING)

Component	Six-Component Spike ⁽¹⁾		Twelve-Component Spike ⁽²⁾	
	Initial ⁽³⁾	Final ⁽⁴⁾	Initial ⁽³⁾	Final ⁽⁴⁾
Phenol	9.36 ± 0.2 ⁽⁵⁾	9.45 ± 0.3	465 ± 18	450 ± 23
2-nitrophenol	- - -	- - -	680 ± 30	710 ± 35
2-chlorophenol	- - -	- - -	627 ± 15	640 ± 9
2,4-dimethylphenol	12.11 ± 0.3	12.5 ± 0.2	615 ± 41	625 ± 27
2,4-dichlorophenol	6.1/2 ⁽⁵⁾ - - -	- - -	795 ± 31	770 ± 42
Dimethyl Phthalate	19.4 ± 0.5	18.9 ± 0.4	941 ± 52	955 ± 38
Diethyl Phthalate	22.0 ± 1.1	21.8 ± 0.6	1102 ± 64	1150 ± 41
Di-n-butyl Phthalate	- - -	- - -	1291 ± 78	1307 ± 61
Acenaphthylene	10.9 ± 0.3	11.0 ± 0.1	744 ± 31	729 ± 36
Phenanthrene	- - -	- - -	910 ± 51	880 ± 41
1,4-dichlorobenzene	14.6 ± 0.2	14.8 ± 0.1	726 ± 28	757 ± 31
Hexachloroethane	- - -	- - -	1110 ± 91	1088 ± 67
COD	193 ± 14	208 ± 15	147 ± 6 ⁽⁶⁾	145 ± 5 ⁽⁶⁾
TOC	40.6 ± 0.9	42.8 ± 1.1	30.7 ± 0.6 ⁽⁶⁾	29.5 ± 0.8 ⁽⁶⁾

- (1) Total storage time = 33 days. Concentrations in mg/l.
 (2) Total storage time = 42 days. Concentrations in µg/l.
 (3) Initial concentration = concentration determined immediately after spiking and prior to initiation of the study.
 (4) Final concentration = concentration determined immediately after completion of the column study.
 (5) Concentrations ± 1 standard deviation for n = 3.
 (6) Concentrations in mg/l.

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The GAC field study on unspiked GCWDA plant effluent was conducted on the second sampling trip (5-29-80) and samples were also collected for use as the matrix for eleven-component spike studies. Two 45 liter carboys were required to complete duplicate runs of the spiked adsorption system. Data on the wastewater background level of spike components for each carboy collected is given in Table 29. Table 30 summarizes the effects of the filtration processes on the concentration of each compound monitored in these studies. Table 31 addresses the issue of spiked wastewater integrity during the storage period required to complete the eleven-component bench scale investigations.

Unfiltered GCWDA final effluent samples collected on the final sampling date, 4-21-81, were used for the site adsorption study performed in the laboratory. Of the eight 45 liter carboys required to complete this study, analyses for selected toxicants were performed on subsamples from the first and last carboys used as column influent. Analysis of the first carboy was conducted at the initiation of the column run, and a subsample from the last carboy used was analyzed just prior to termination of the study. Results of these analyses are presented in Table 32.

A two-tailed t-test for unpaired data was the statistic used for evaluation of sample means. This parameter was used to determine whether statistically significant differences existed between mean concentrations of individual compounds at the 95% significance level. t-test calculations were performed on the mean concentration of each compound (or parameter) in the following series of samples: 1) background level of carboy 1 vs carboy 2 for each sampling date; 2) unfiltered vs sand filtered for each sampling date; 3) unfiltered vs membrane filtered for each sampling date; 4) sand filtered vs membrane filtered for each sampling date; 5) initial vs final spike concentration for six, eleven, and twelve-component matrices; 6) initial spike concentration of carboy 1 vs carboy 2 for the eleven component matrix; and, 7) initial carboy vs final carboy for the 4-21-81 site study.

A statistically significant difference in mean concentration was not detected for any compound in any of the comparisons performed. Results of these statistical analyses indicate that no significant change in component concentration resulted from the filtration processes, that replicate sample background and spike concentration levels were equivalent, and that no significant change in compound concentration resulted from sample storage. However, it should be noted that these findings are undoubtedly largely a function of the small sample size (n=3 in all cases). With this sample size, relatively large variation in replicate observations is required for the t-test to detect differences in sample means at the 95% significance level. Thus, these data should not be interpreted to mean that no differences exist, but rather that differences could not be verified statistically.

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TABLE 29. SPIKE COMPONENT BACKGROUND LEVELS FOR 5-29-80 WASTEWATER SAMPLES⁽¹⁾

Component	Conc. Carboy 1 ($\mu\text{g/l}$)	Conc. Carboy 2 ($\mu\text{g/l}$)
Phenol ⁽²⁾	$1.1 \pm 0.3^{(3)}$	2.2 ± 1.7
2-nitrophenol	1.4 ± 0.5	1.9 ± 0.9
2-chlorophenol ⁽²⁾	1.2 ± 0.7	1.2 ± 0.8
2,4-dimethylphenol ⁽²⁾	1.6 ± 0.4	2.1 ± 0.7
2,4-dichlorophenol ⁽²⁾	14.3 ± 1.1	16.1 ± 2.4
Dimethyl Phthalate ⁽²⁾	27.3 ± 2.6	30.2 ± 2.5
Diethyl Phthalate ⁽²⁾	34.4 ± 3.1	31.9 ± 1.8
Di-n-butyl Phthalate ⁽²⁾	7.3 ± 2.2	9.5 ± 3.1
Acenaphthylene ⁽²⁾	8.9 ± 2.6	8.0 ± 1.9
1,4-dichlorobenzene ⁽²⁾	5.6 ± 1.6	4.3 ± 2.7
1,1,2,2-tetrachloroethane	7.2 ± 3.1	6.5 ± 2.2
COD ⁽⁴⁾	121 ± 9	116 ± 4
TOC ⁽⁴⁾	26.0 ± 1.6	25.1 ± 1.1

- (1) Values for membrane filtered wastewater samples.
 (2) Presence in both carboys verified by mass spectrometry.
 (3) Values are means $\pm$ 1 standard deviation for $n = 3$.
 (4) Concentrations in mg/l.

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TABLE 30. EFFECTS OF FILTRATION ON UNSPIKED WASTEWATER (5-29-80 SAMPLING)⁽¹⁾

Component	Concentration (µg/l)		
	Unfiltered	Sand Filtered	Membrane Filtered
Phenol	1.1 ± 0.4 ⁽²⁾	1.2 ± 0.5	1.1 ± 0.3
2-nitrophenol	1.6 ± 0.4	1.4 ± 0.6	1.4 ± 0.5
2-chlorophenol	1.4 ± 0.6	<1.0	1.2 ± 0.7
2,4-dimethylphenol	2.2 ± 0.5	1.8 ± 0.3	1.6 ± 0.4
2,4-dichlorophenol	16.7 ± 0.8	13.8 ± 1.3	14.3 ± 1.1
Dimethyl Phthalate	31.1 ± 0.9	25.9 ± 2.2	27.3 ± 2.6
Diethyl Phthalate	40.6 ± 3.7	36.6 ± 4.2	34.4 ± 3.1
Di-n-butyl Phthalate	6.9 ± 2.5	7.1 ± 1.6	7.3 ± 2.2
Acenaphthylene	9.1 ± 1.7	8.2 ± 1.1	8.9 ± 2.6
1,4-dichlorobenzene	6.3 ± 0.8	6.0 ± 1.2	5.6 ± 1.6
1,1,2,2-tetrachloroethane	9.7 ± 1.2	9.1 ± 1.4	7.2 ± 3.1
2,4,6-trichlorophenol ⁽³⁾	5.8 ± 1.1	6.1 ± 1.3	- - -
4,6-dinitro-o-cresol	977 ± 101	922 ± 89	- - -
Acenaphthene	1.3 ± 0.7	1.4 ± 0.5	- - -
Fluorene	2.4 ± 0.8	2.0 ± 1.0	- - -
Anthracene	2.9 ± 0.5	2.9 ± 0.9	- - -
Phenanthrene	1.2 ± 0.9	1.7 ± 1.2	- - -
Pyrene	<1	<1	- - -
TOC ⁽⁴⁾	163 ± 8	151 ± 5	121 ± 9
COD ⁽⁴⁾	28.3 ± 0.5	27.1 ± 0.8	26.0 ± 1.6

(1) Values presented are for carboy 1.

(2) Values are means ± standard deviation for n = 3.

(3) 2,4,6-trichlorophenol through pyrene were monitored only in the field study. Sand filtered wastewater served as the influent to the field study carbon column.

(4) Concentrations in mg/l.

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TABLE 31. STORAGE EFFECTS ON SPIKED WASTEWATER (5-29-80 SAMPLING)⁽¹⁾

Component	Spike Component Concentration ⁽²⁾			
	Carboy 1		Carboy 2	
	Initial ⁽³⁾	Final ⁽⁴⁾	Initial ⁽³⁾	Final ⁽⁴⁾
Phenol	457 ± 29	451 ± 12	477 ± 10	495 ± 22
2-nitrophenol	715 ± 28	730 ± 20	683 ± 18	695 ± 32
2-chlorophenol	633 ± 6	626 ± 5	660 ± 20	650 ± 15
2,4-dimethylphenol	608 ± 60	596 ± 23	623 ± 32	620 ± 46
2,4-dichlorophenol	788 ± 41	812 ± 17	816 ± 2	826 ± 12
Dimethyl Phthalate	875 ± 51	927 ± 62	939 ± 41	930 ± 56
Diethyl Phthalate	1086 ± 88	1125 ± 28	1125 ± 60	1108 ± 37
Di-n-butyl Phthalate	1433 ± 95	1373 ± 41	1389 ± 81	1364 ± 30
Acenaphthylene	758 ± 44	763 ± 54	758 ± 54	755 ± 29
1,4-dichlorobenzene	706 ± 9	714 ± 12	698 ± 11	703 ± 15
1,1,2,2-tetrachloroethane	814 ± 22	805 ± 14	821 ± 37	806 ± 27
COD ⁽⁵⁾	131 ± 9	134 ± 7	126 ± 4	122 ± 8
TOC ⁽⁵⁾	28.0 ± 1.6	28.4 ± 1.3	27.3 ± 1.4	26.8 ± 0.9

(1) Total storage time = 44 days.

(2) Values are means ± 1 standard deviation for n = 3 (µg/l).

(3) Initial concentration is value obtained from samples extracted immediately after spike addition to the carboy indicated.

(4) Final concentration is the value obtained from samples extracted upon depletion of the carboy indicated.

(5) Concentrations in mg/l.

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TABLE 32. WASTEWATER TOXICANT LEVELS FOR 4-21-81 SITE STUDY

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Compound	Concentration ($\mu\text{g/l}$) ⁽¹⁾	
	Initial Carboy ⁽²⁾	Final Carboy ⁽³⁾
Phenol	0.7 ± 0.3	0.9 ± 0.5
2-nitrophenol	0.6 ± 0.4	1.0 ± 0.3
2-chlorophenol	1.1 ± 0.4	1.5 ± 0.7
2,4-dimethylphenol	11.0 ± 1.2	9.8 ± 2.0
2,4-dichlorophenol	6.1 ± 1.4	5.7 ± 1.2
2,4,6-trichlorophenol	4.7 ± 2.1	3.6 ± 2.4
4,6-dinitro-o-cresol	1196 ± 151	1272 ± 111
Dimethyl Phthalate	0.9 ± 0.6	1.2 ± 0.7
Diethyl Phthalate	1.3 ± 0.4	2.4 ± 1.1
Di-n-butyl Phthalate	3.7 ± 1.2	3.1 ± 2.4
1,4-dichlorobenzene	1.0 ± 0.6	0.9 ± 0.2
Acenaphthene	0.7 ± 0.3	1.1 ± 0.5
Acenaphthylene	1.0 ± 0.9	2.1 ± 1.3
Phenanthrene	<0.5	<0.5
Anthracene	2.7 ± 1.6	3.4 ± 1.9
Fluorene	2.2 ± 1.4	4.2 ± 2.1
Pyrene	ND ⁽⁴⁾	ND ⁽⁴⁾

(1) Concentration values given ± 1 standard deviation for $n = 3$.

(2) Initial carboy = the first carboy used as carbon column influent (of 8 used in total).

(3) Final carboy = the last (eighth) carboy used as carbon column influent. Total storage time until depletion of this carboy = 100 hours.

(4) ND = none detected.

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BENCH ADSORPTION STUDIES

Single And Six-Solute Adsorption Matrices

Results obtained from single component and six-component DIW adsorption systems are summarized in Table 33, with initial breakpoints and capacity reductions from competitive adsorption noted. These data are presented

TABLE 33. ADSORPTION CHARACTERISTICS FROM SINGLE AND SIX-SOLUTE DIW MATRICES

Component	Single-Solute Matrix		Six-Solute Matrix	
	Initial BP ⁽¹⁾ (Bed Volumes)	Max.Capacity (mM/g)	Initial BP ⁽¹⁾ (Bed Volumes)	Max.Capacity ⁽²⁾ (mM/g)
Phenol	2735	1.19	365	0.28 (76)
2,4-dimethylphenol	3713	2.63	365	0.51 (80)
Dimethyl Phthalate	4841	1.62	<195	0.45 (72)
Diethyl Phthalate	5283	1.94 ⁽³⁾	365	0.75 ⁽⁴⁾ (61)
Acenaphthylene	3550	>>0.92 ⁽³⁾	365	----- ⁽⁴⁾
1,4-dichlorobenzene	6739	>4.5 ⁽³⁾	874	----- ⁽⁴⁾

(1) BP = breakpoint.

(2) Values in parentheses are percentage reductions in adsorptive capacity.

(3) Actual maximum values not determined in column run times used.

(4) Column run times too short to determine these values.

graphically as cumulative mass of solute adsorbed per unit mass of carbon versus cumulative volume of water treated in Figures 4-9. Inflections are indicative of the column breakpoints for each solute.

Results obtained when these same six solutes were spiked into the wastewater matrix are shown graphically in Figure 10. The difference in the slope of the adsorption curve for acenaphthylene results from a slightly lower influent concentration (Table 14). Table 34 depicts differences in adsorption characteristics for each solute from six-component DIW and wastewater matrices.

Eleven-And Twelve-Solute Adsorption Matrices

In subsequent studies, DIW and wastewater matrices were spiked with additional organic toxicants, but at significantly lower (20X lower) concentration levels. These adsorption systems were used to further investigate the effects of matrix complexity on adsorptive phenomena, and to evaluate the effectiveness of TOC/COD column monitoring parameters.

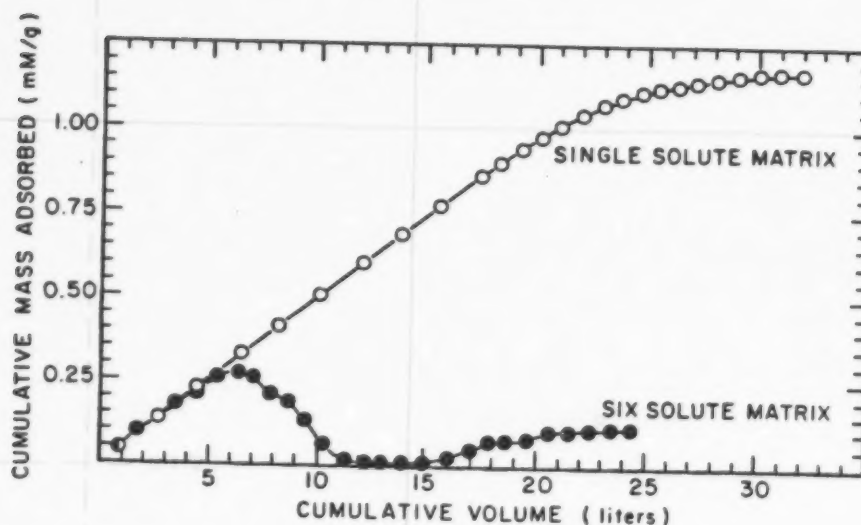


Figure 4. Adsorption of phenol from single and six-solute deionized water matrices.

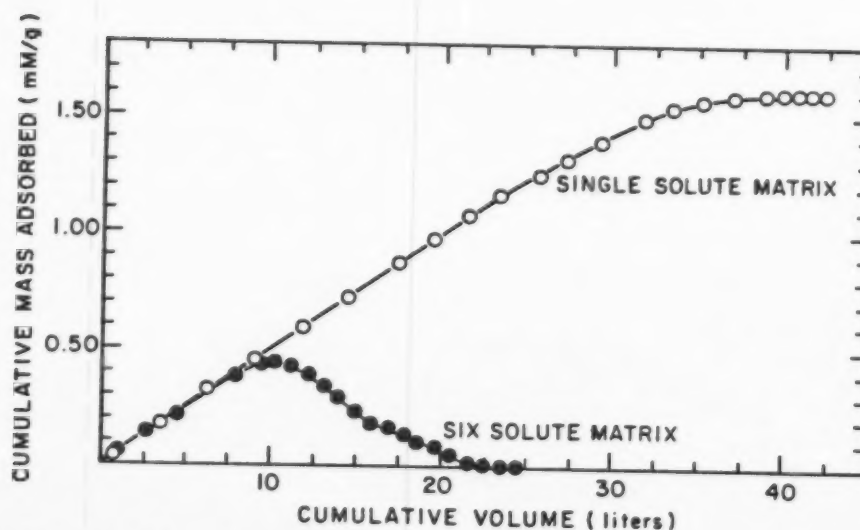


Figure 5. Adsorption of dimethyl phthalate from single and six-solute deionized water matrices.

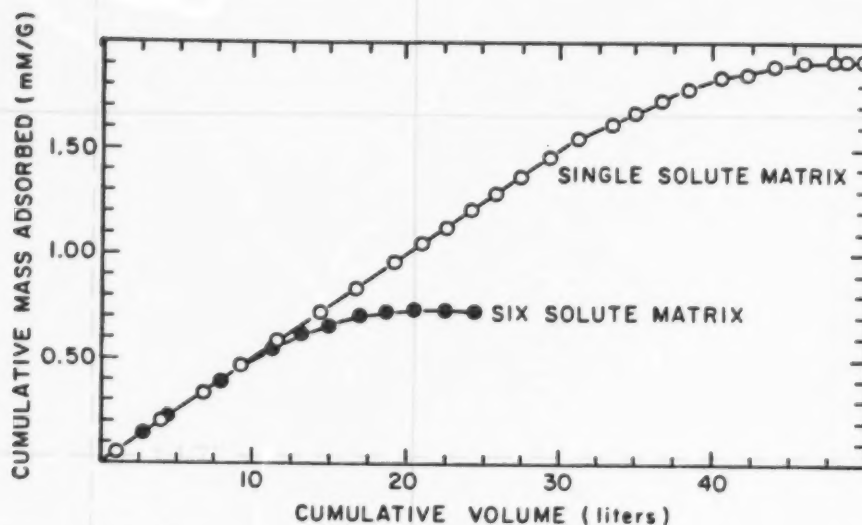


Figure 6. Adsorption of diethyl phthalate from single and six-solute deionized water matrices.

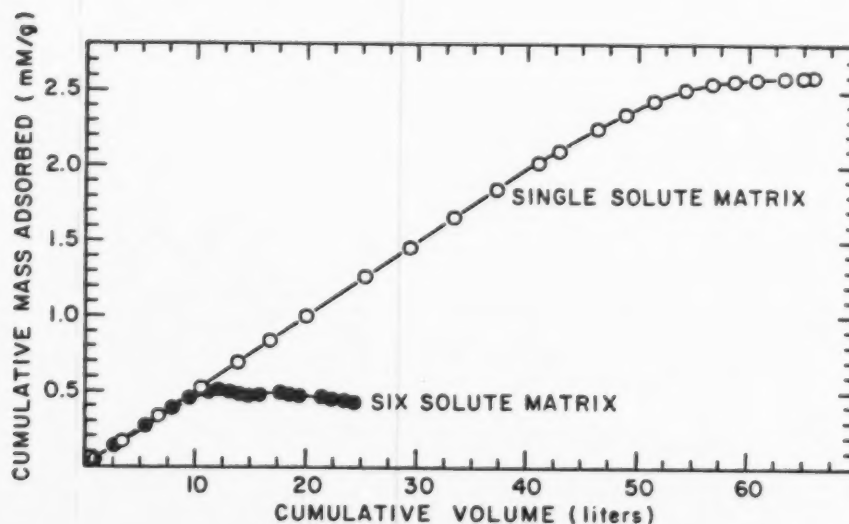


Figure 7. Adsorption of 2,4-dimethylphenol from single and six-solute deionized water matrices.

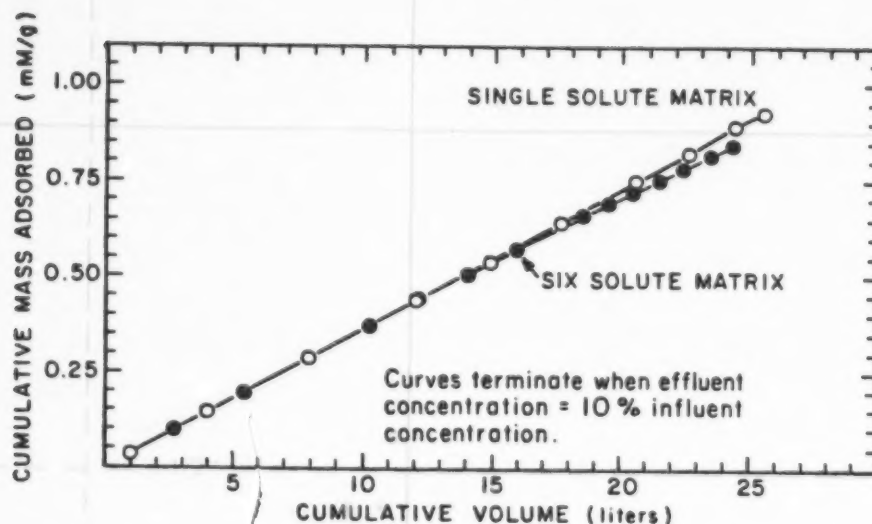


Figure 8. Adsorption of acenaphthylene from single and six-solute deionized water matrices,

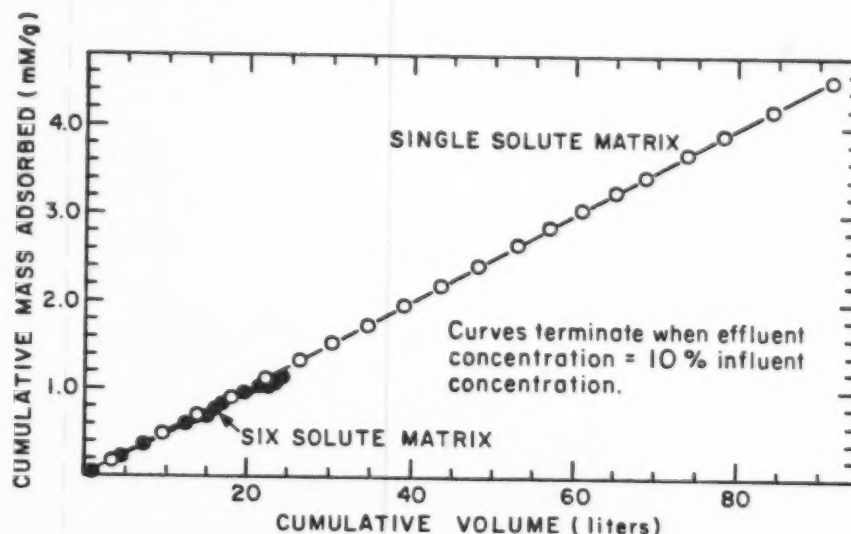


Figure 9. Adsorption of 1,4-dichlorobenzene from single and six-solute deionized water matrices,

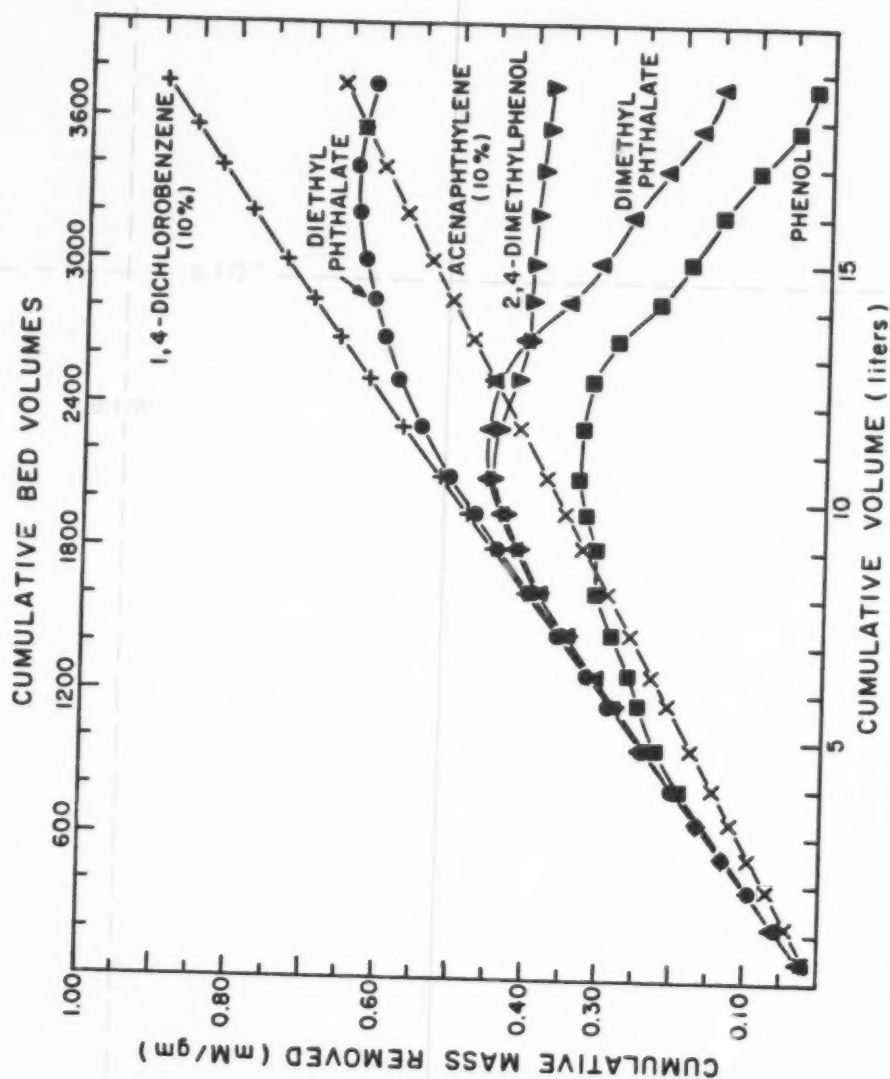


Figure 10. Adsorption competition between six solutes spiked into a combined industrial wastewater matrix.

TABLE 34. ADSORPTION CHARACTERISTICS FROM SIX-SOLUTE MATRICES

Component	DIW Matrix		Wastewater Matrix	
	Initial BP ⁽¹⁾ (Bed Volumes)	Max. Capacity (mM/g)	Initial BP ⁽¹⁾ (Bed Volumes)	Max. Capacity (mM/g)
Phenol	365	0.28	<87 ⁽²⁾	0.31
2,4-dimethylphenol	365	0.51	231	0.45
Dimethyl Phthalate	<195 ⁽²⁾	0.45	<87 ⁽²⁾	0.45
Diethyl Phthalate	365	0.75	<87 ⁽²⁾	0.64 ⁽³⁾
Acenaphthylene	365	0.85 ⁽³⁾	<87 ⁽²⁾	0.66 ⁽³⁾
1,4-dichlorobenzene	874	1.08 ⁽³⁾	380	0.82 ⁽³⁾

(1) BP = breakpoint.

(2) Less than symbol indicates compound appeared in the first effluent fraction collected, which occurred at the volume given.

(3) Carbon capacity at approximately 10% breakthrough.

Lower spike concentration levels necessitated longer column run times for these studies, particularly in DIW matrices. Column runs were maintained for a time period sufficient to allow near complete breakthrough of low affinity components and to define the shapes of the breakthrough curves for all spike constituents. Key breakthrough parameters from twelve-component DIW and wastewater adsorption matrices are summarized in Tables 35 and 36, respectively. Breakthrough curves for selected solutes from the twelve-component wastewater matrix are presented graphically in Figure 11. Breakthrough data for the eleven-component DIW and wastewater matrices are listed in Tables 37 and 38 respectively, and complete breakthrough data are provided subsequently (see Figures 18-28).

TOC/COD Breakthrough Results

TOC and COD determinations were made on all carbon column effluent fractions collected in both eleven- and twelve-component wastewater matrix studies. COD measurements were made both by the standard potassium dichromate digestion procedure, and by correlation with UV absorption values at 240 nm. Breakthrough curves for these parameters were used for comparison with breakthrough curves for specific toxicants to evaluate utility as carbon performance indicators. The breakthrough curves for TOC, COD (UV correlation), and COD (digestion) from the twelve-component wastewater matrix are presented in Figures 12-14, respectively. Breakthrough curves for these parameters from the eleven-component wastewater matrix are shown in Figures 15-17.

TABLE 35. SOLUTE BREAKTHROUGH CHARACTERISTICS FROM TWELVE-COMPONENT DIW MATRIX

Component	Initial BP ⁽¹⁾		~10% BP ⁽¹⁾		Run Termination (8560 BV's)	
	(Bed Volumes)	Bed Volumes	Cum. Capacity	(2)	%BT	Cum. Capacity (2)
Phenol	3751	5530	69.16		31.9	101.44
2-nitrophenol	4299	7008	87.03		14.1	103.70
2-chlorophenol	4484	--	---		9.5	106.01
2,4-dimethylphenol	5878	--	---		1.7	107.04
2,4-dichlorophenol	5878	--	---		2.2	106.90
Dimethyl Phthalate	2295	--	---		5.3	106.16
Diethyl Phthalate	2295	--	---		4.7	106.46
Di-n-butyl Phthalate	2295	--	---		4.7	106.61
Acenaphthylene	5689	--	---		6.5	107.18
Phenanthrene	5878	--	---		1.8	107.25
1,4-dichlorobenzene	5530	--	---		7.5	106.83
Hexachloroethane	5530	--	---		5.8	106.70

(1) BP - breakpoint.
(2) Cumulative carbon capacity at breakpoint indicated in $\mu\text{M/g}$.

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TABLE 36. SOLUTE BREAKTHROUGH CHARACTERISTICS FROM TWELVE-COMPONENT WASTEWATER MATRIX

Component	Initial Bp ⁽¹⁾ (Bed Volumes)	~10% Bp (2)			~25% Bp (2)		~50% Bp (2)		Run Termination (3)	
									%BT	Cum. Capacity (4)
Phenol	524	1808(22.13)	2877(33.54)	3494(38.43)	147.0	41.30(43.31)	(5)			
2-nitrophenol	524	2138(25.78)	2694(31.70)	3237(36.55)	160.6	37.56(41.11)	(5)			
2-chlorophenol	710	2694(32.86)	3237(38.52)	4232(46.00)	103.2	50.08(50.31)	(5)			
2,4-dimethylphenol	710	3058(37.11)	3841(45.22)	5350(57.19)	81.6	58.09				
2,4-dichlorophenol	710	3058(36.74)	4025(47.17)	5531(59.84)	63.9	61.87				
Dimethyl Phthalate	524	1808(21.25)	3384(36.75)	4575(45.23)	100.5	48.94				
Diethyl Phthalate	524	2694(32.08)	4025(45.57)	5351(56.33)	74.0	57.76				
Di-n-butyl Phthalate	524	-----	-----	-----	0.8	71.72				
Acenaphthylene	1808	5531(66.49)	-----	-----	13.9	68.57				
Phenanthrene	2538	-----	-----	-----	3.9	70.97				
1,4-dichlorobenzene	2003	5734(68.98)	-----	-----	11.0	68.98				
Hexachloroethane	1808	-----	-----	-----	5.1	70.12				

(1) BP = breakpoint.

(2) Breakpoint indicated in bed volumes treated with cumulative carbon capacity in $\mu\text{M/g}$ given in parentheses.

(3) Run terminated at 5734 bed volumes treated.

(4) Cumulative carbon capacity at 5734 bed volumes treated in $\mu\text{M/g}$.

(5) Maximum capacity attained in parentheses.

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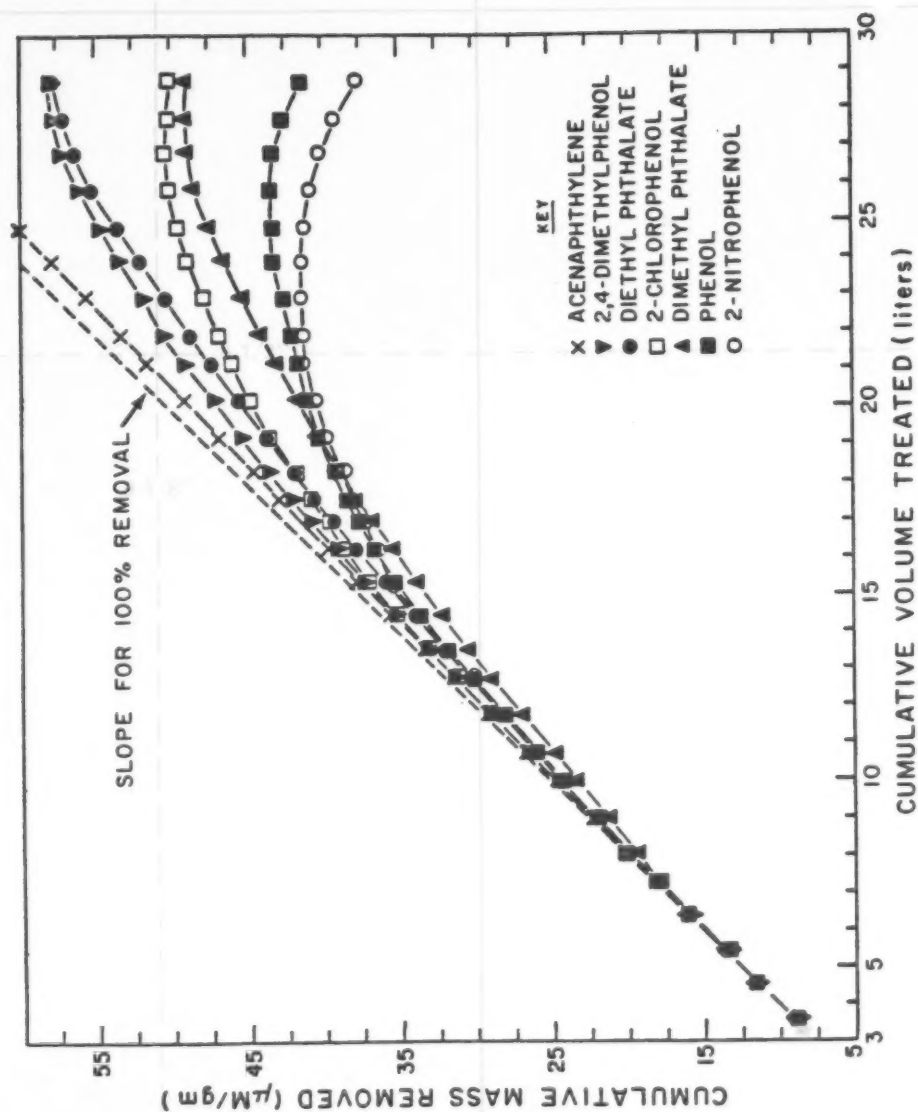


Figure 11. Breakthrough of selected toxicants from twelve-component wastewater matrix.

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TABLE 37. SOLUTE BREAKTHROUGH CHARACTERISTICS FROM ELEVEN-COMPONENT DIW MATRIX

Component	Initial Bp ⁽¹⁾		Run Termination ⁽³⁾		Cum. Capacity ⁽⁴⁾	Run Termination ⁽⁵⁾
	(Bed Volumes)	~10% Bp ⁽²⁾	~25% Bp ⁽²⁾	~50% Bp ⁽²⁾	%BT	
Phenol	3875	6299(78.25)	8040(96.33)	9378(106.67)	117.4	111.76(112.19)
2-nitrophenol	4661	7233(89.81)	9378(112.37)	10807(122.93)	54.5	124.06
2-chlorophenol	4847	9181(112.98)	11006(131.86)	-----	23.5	131.86
2,4-dimethylphenol	6299	-----	-----	-----	2.2	137.52
2,4-dichlorophenol	6299	-----	-----	-----	2.3	136.63
Dimethyl Phthalate	2370	11006(134.70)	-----	-----	9.2	134.70
Diethyl Phthalate	2370	-----	-----	-----	8.7	135.29
Di-n-butyl Phthalate	2195	-----	-----	-----	7.6	135.19
Acenaphthylene	6139	11006(134.43)	-----	-----	9.9	137.43
1,4-dichlorobenzene	5769	-----	-----	-----	5.0	136.50
1,1,2,2-tetrachloroethane	1044	6894(84.69)	8416(100.18)	9789(110.51)	68.7	116.46

- (1) BP = breakpoint.
 (2) Breakpoint indicated in bed volumes treated with cumulative carbon capacity in $\mu\text{M/g}$ given in parentheses.
 (3) Run was terminated at 11006 bed volumes treated.
 (4) Cumulative carbon capacity at 11006 bed volumes treated in $\mu\text{M/g}$.
 (5) Maximum capacity attained in parentheses.

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TABLE 38. SOLUTE BREAKTHROUGH CHARACTERISTICS FROM ELEVEN-COMPONENT WASTEWATER MATRIX

Component	Initial Bp (1) (Bed Volumes)	~10% BP (2)			~25% BP (2)		~50% BP (2)		Run Termination (3) %BT Cum. Capacity (4)	
Pheno1	765								1.3	84.84
2-nitropheno1	365	1900(23.08)	2279(26.73)	2604(29.02)	2604(29.02)	2604(29.02)	2604(29.02)	2604(29.02)	156.3	21.01(32.81)
2-chloropheno1	976	2604(31.84)	2964(35.25)	5464(53.55)	5464(53.55)	5464(53.55)	5464(53.55)	5464(53.55)	81.2	58.69
2,4-dimethylpheno1	976	2783(33.92)	3687(42.86)	6215(62.33)	6215(62.33)	6215(62.33)	6215(62.33)	6215(62.33)	61.1	65.70
2,4-dichloropheno1	1161	2783(33.65)	3888(44.76)	5651(58.42)	5651(58.42)	5651(58.42)	5651(58.42)	5651(58.42)	66.5	64.60
Dimethyl Phthalate	765								1.2	84.97
Diethyl Phthalate	365								2.0	84.77
Di-n-butyl Phthalate	365								< 1	85.33
Acenaphthylene	2086								8.3	83.32
1,4-dichlorobenzene	1717	6422(77.47)							12.4	81.90
1,1,2,2-tetrachloroethane	191	1717(20.61)	2604(29.24)	2964(31.48)	2964(31.48)	2964(31.48)	2964(31.48)	2964(31.48)	100.8	40.00

- (1) BP = breakpoint.
 (2) Breakpoint indicated in bed volumes treated with cumulative carbon capacity in $\mu\text{M/g}$ given in parentheses.
 (3) Run was terminated at 6823 bed volumes treated.
 (4) Cumulative carbon capacity at 6823 bed volumes treated in $\mu\text{M/g}$.
 (5) Maximum capacity attained in parentheses.

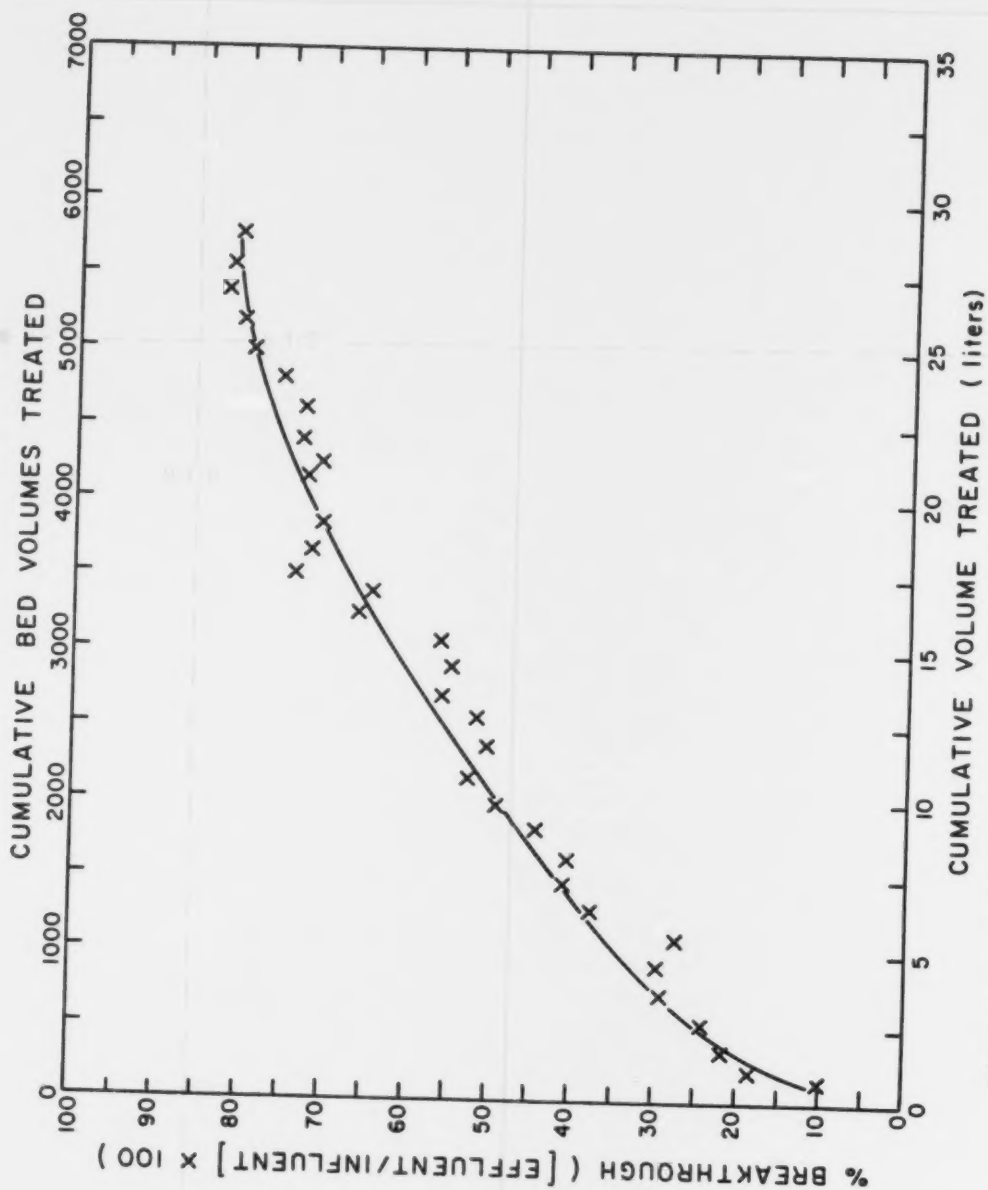


Figure 12. TOC breakthrough from twelve-component wastewater matrix.

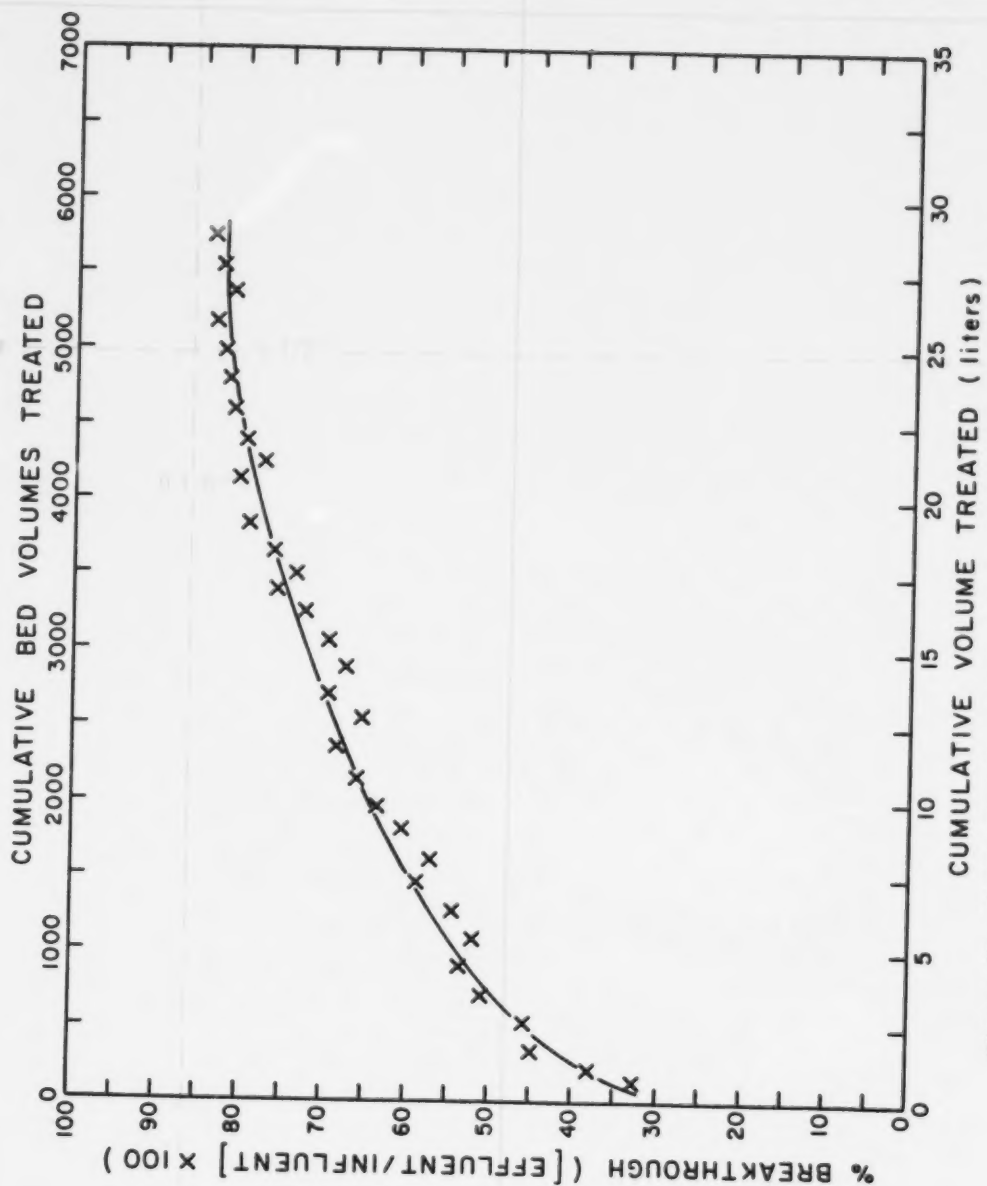


Figure 13. COD (UV Correlation) breakthrough from twelve-component wastewater matrix.

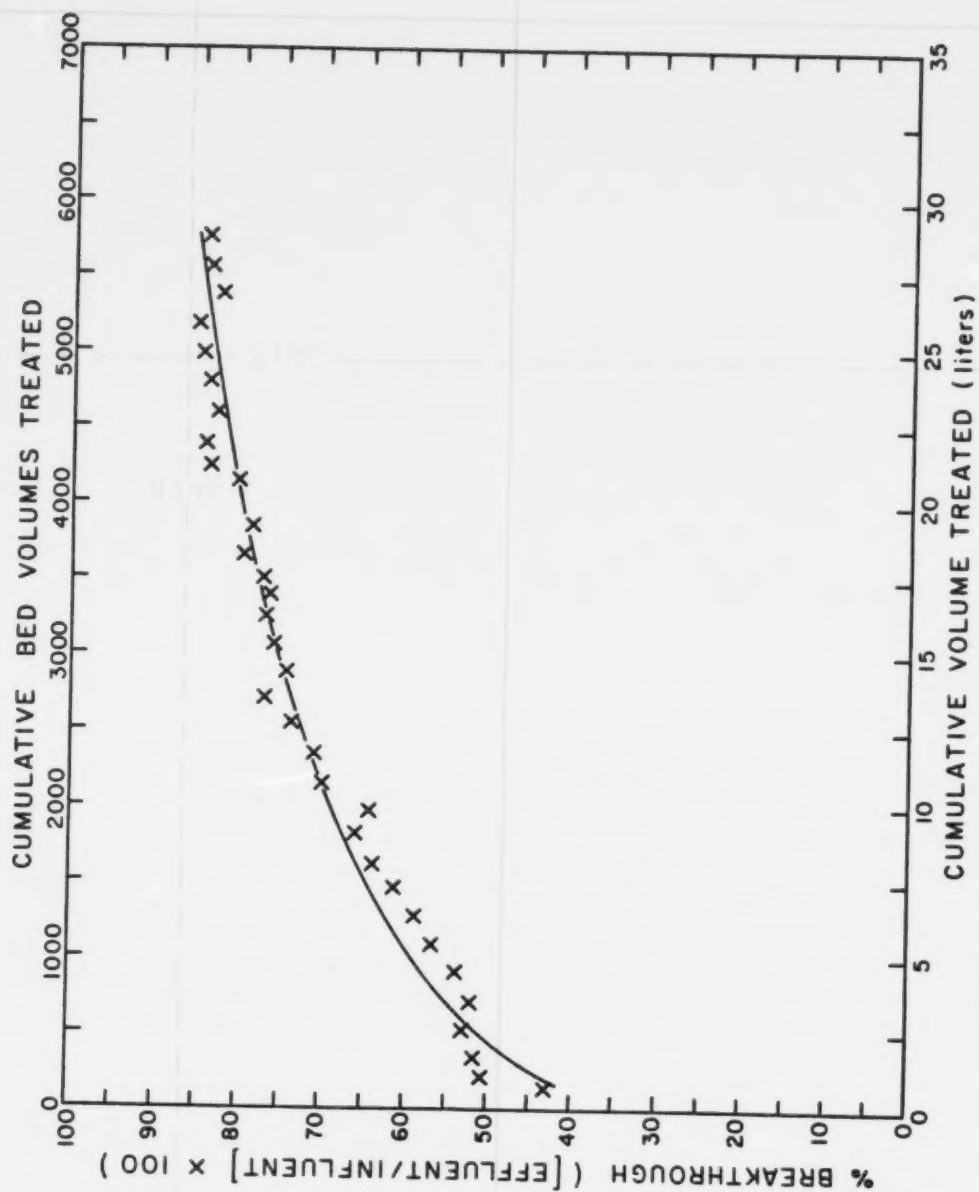


Figure 14. COD (Digestion) breakthrough from twelve-component wastewater matrix.

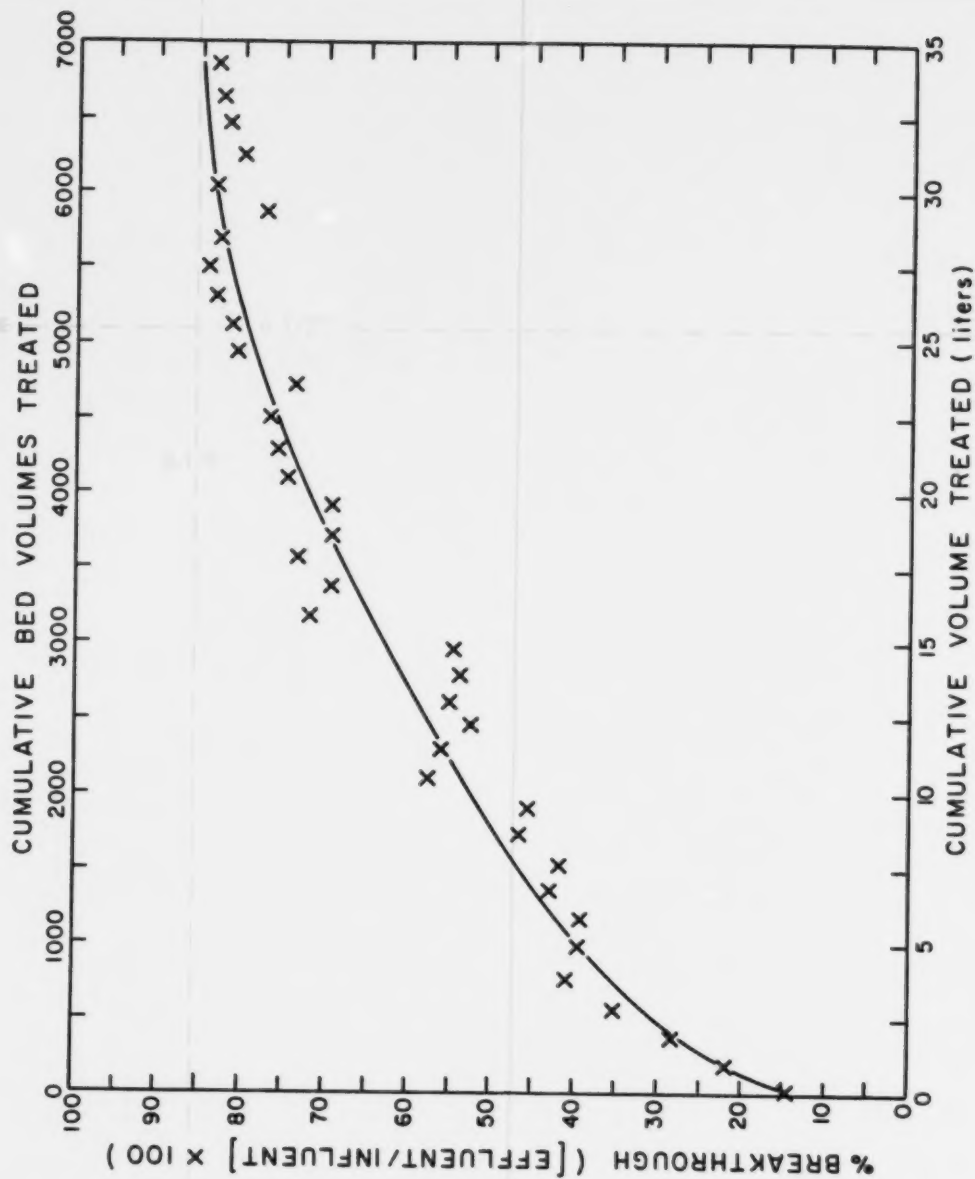


Figure 15. TOC breakthrough from eleven-component wastewater matrix.

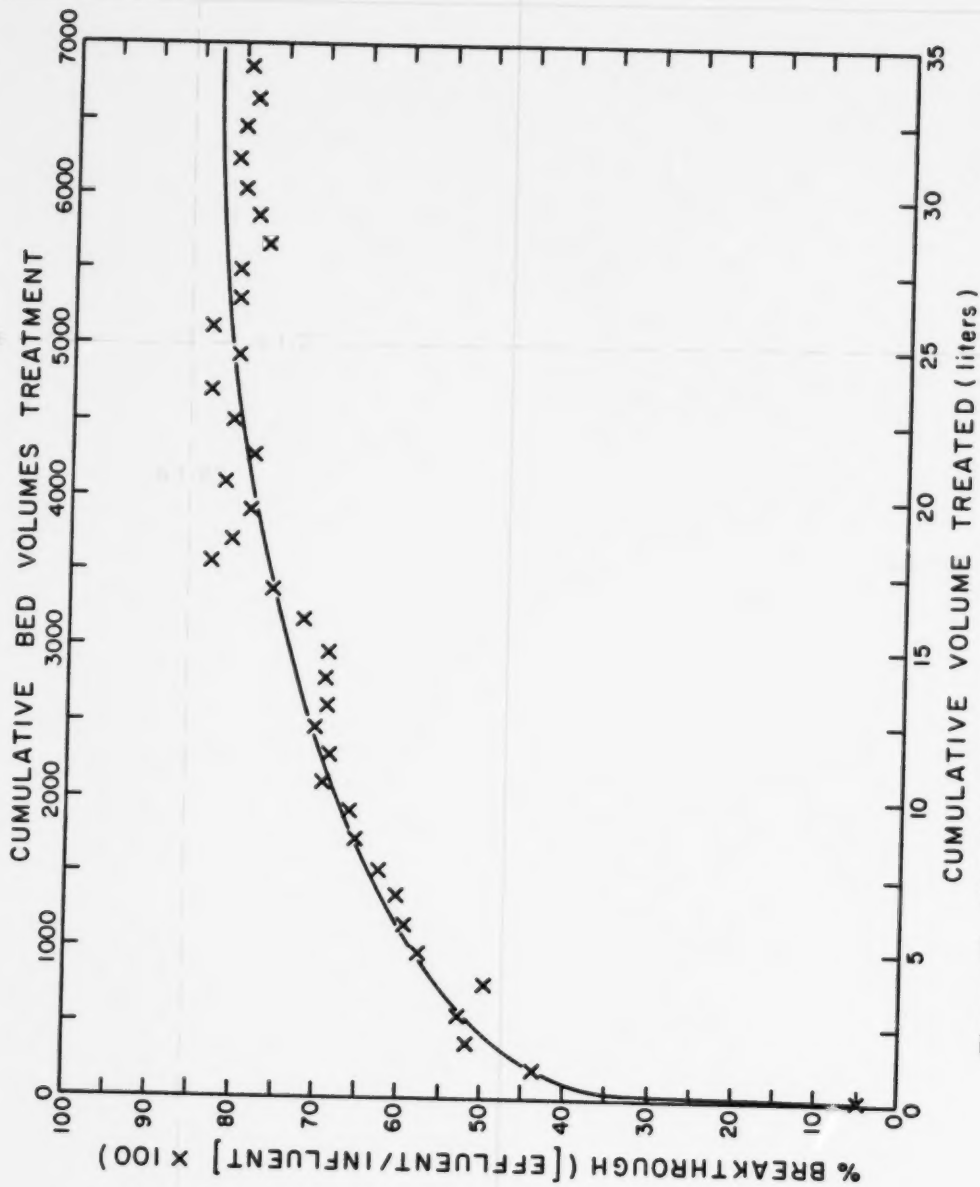


Figure 16. COD (UV Correlation) breakthrough from eleven-component wastewater matrix.

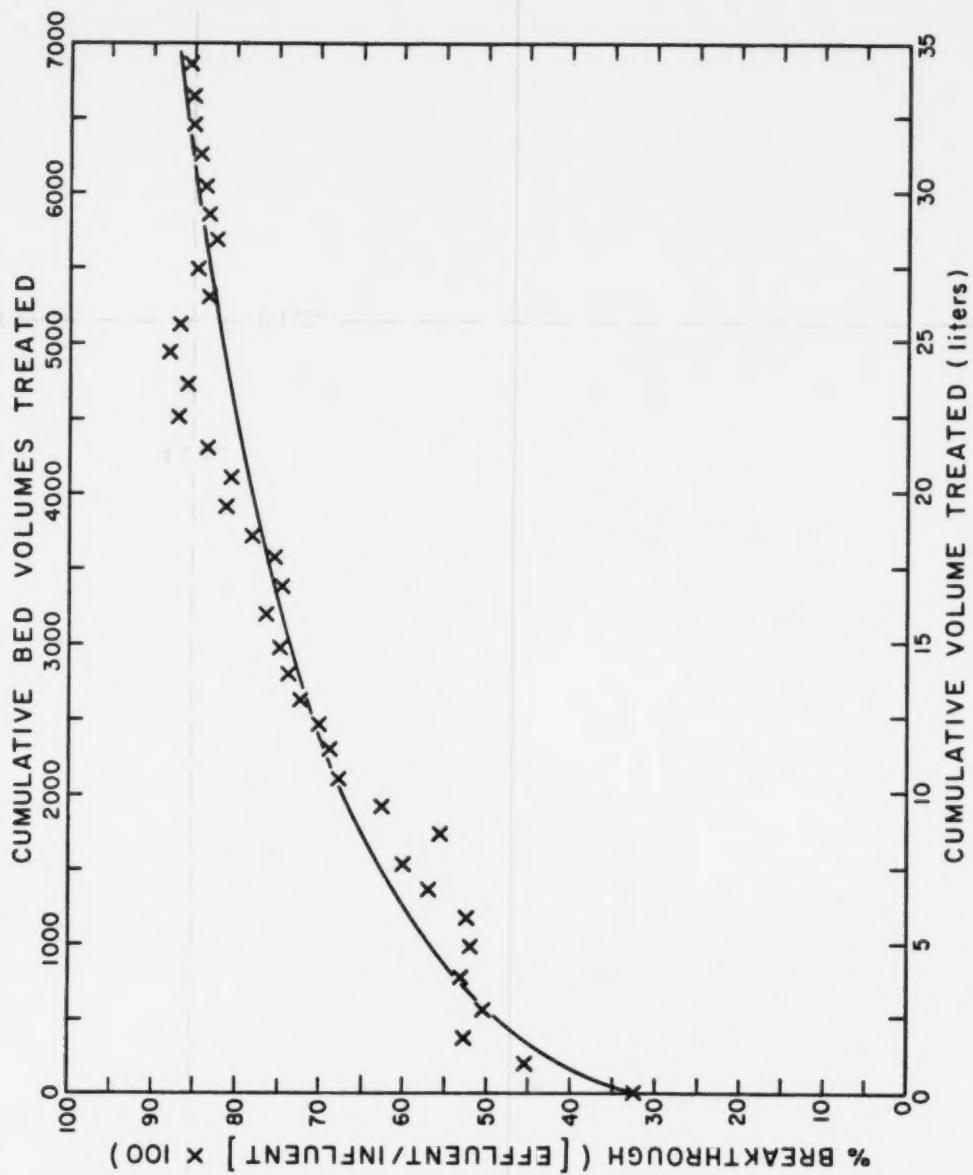


Figure 17. COD (Digestion) breakthrough from eleven-component wastewater matrix.

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Carbon Comparison Studies

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The eleven-component DIW adsorption matrix was also used for comparison of adsorptive properties of three different active carbons, and for evaluation of column run reproducibility. Carbons selected for this portion of the study include: 1) virgin Calgon Filtrasorb 400 (a coal based active carbon); 2) regenerated Calgon Filtrasorb 400; and, 3) virgin Witco 950 (a petroleum based active carbon). All experimental parameters were held constant, so that the only variation was the active carbon material itself. Complete breakthrough data for these carbons are provided in Figures 18-28, along with similar data for the comparable wastewater run.

Virgin Calgon Filtrasorb 400 was used to examine reproducibility, with duplicate runs made for both the eleven-component DIW and wastewater matrices. Data for selected breakthrough parameters from replicate DIW and wastewater runs are summarized in Tables 39 and 40, respectively. Complete breakthrough data for duplicate DIW and wastewater runs are presented in the Appendix (Table A1-A11).

SITE STUDIES

Analyses of carbon column effluent samples from the 5-80 site study revealed that no breakthrough of study toxicants had occurred within the duration of the column run (268 bed volumes). Carbon samples from the column used in this study were extracted and analyzed for selected toxicants using GLC techniques. Data pertinent to sectioning and extraction of the carbon column is presented in Table 41. Results from these analyses were used to examine toxicant movement within the carbon column. These data are presented graphically as plots of fraction number (sample position in the carbon column) vs. mass of toxicant adsorbed per unit mass of activated carbon in Figure 29. These data are semi-quantitative, in that plotted values are uncorrected for extraction efficiency.

TABLE 41. CARBON COLUMN EXTRACTION DATA FOR THE 5-80 SITE STUDY

Fraction No. (1)	Approximate Section Thickness(cm)	Mass Of Carbon In Section (g)	Mass of Carbon Extracted(g)
1	0.5	12.1	12.1
2	1.0	16.3	16.3
3	1.0	20.0	20.0
4	2.0	45.1	45.1
5	2.5	55.7	18.6
6	4.0	76.4	20.9
7	10.0	199.4	53.4

(1) Fraction 1 is from the top (influent) end of the carbon column, and fraction 7 is from the bottom (effluent) end.

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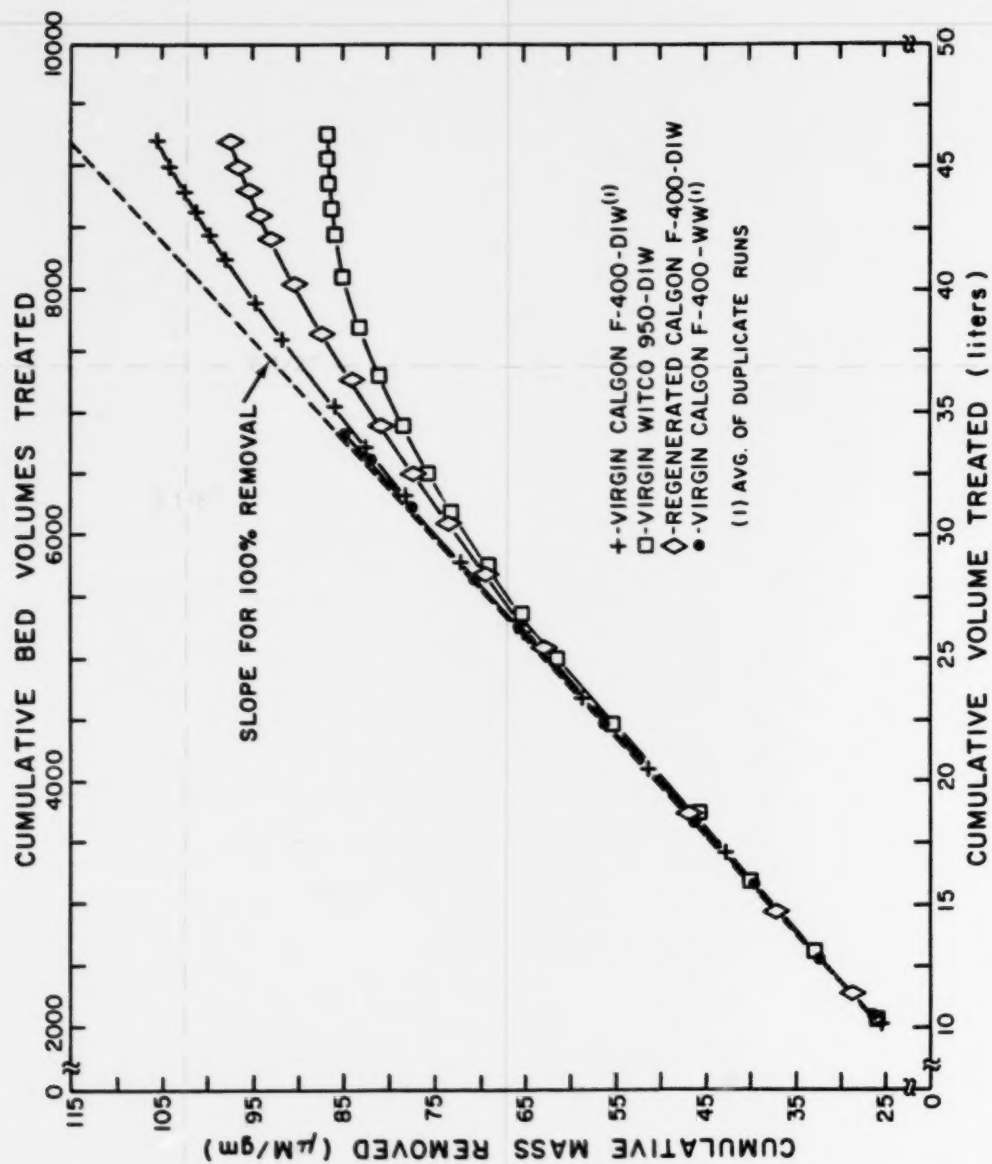


Figure 18. Breakthrough curves for Phenol.

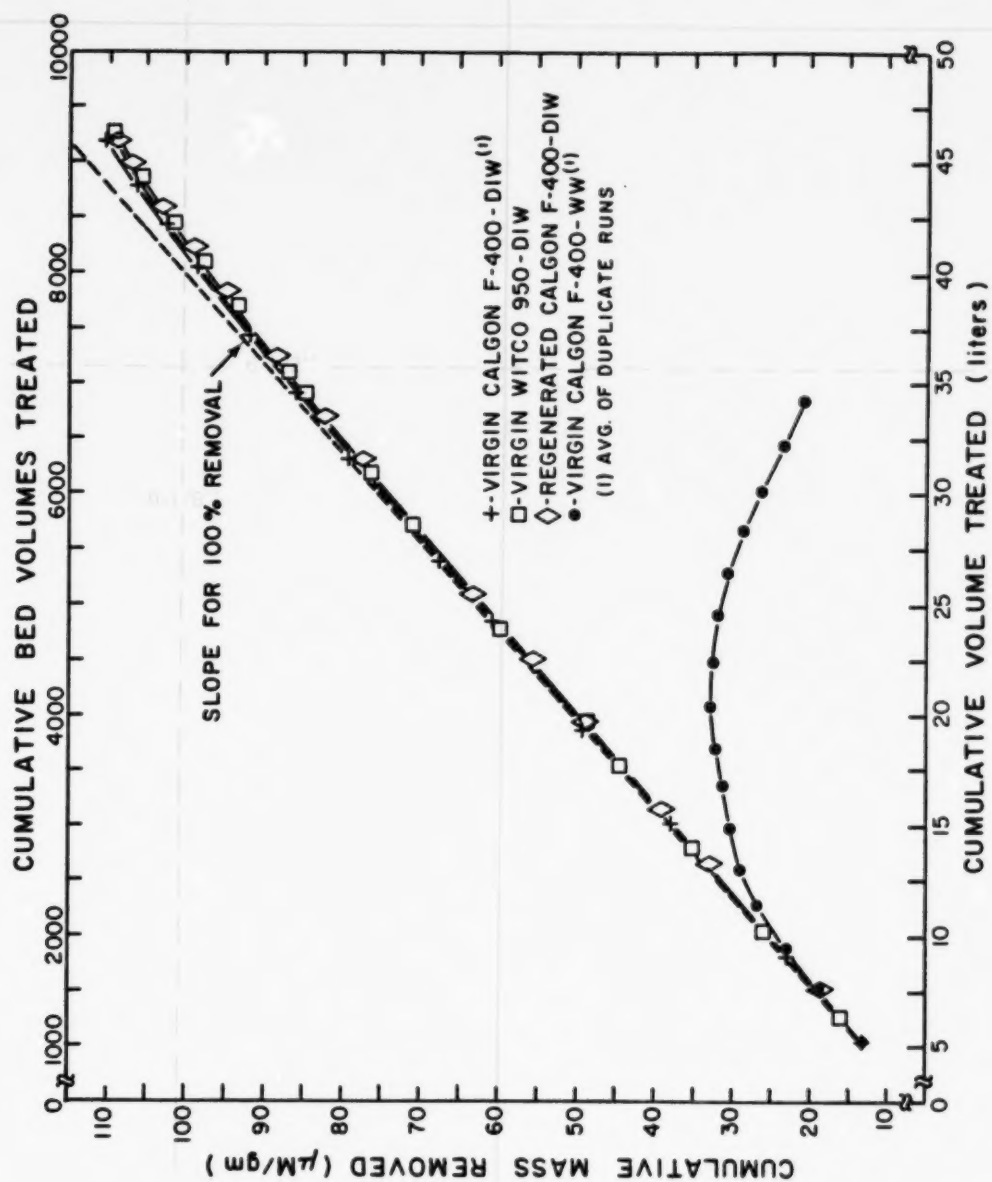


Figure 19. Breakthrough curves for 2-Nitrophenol.

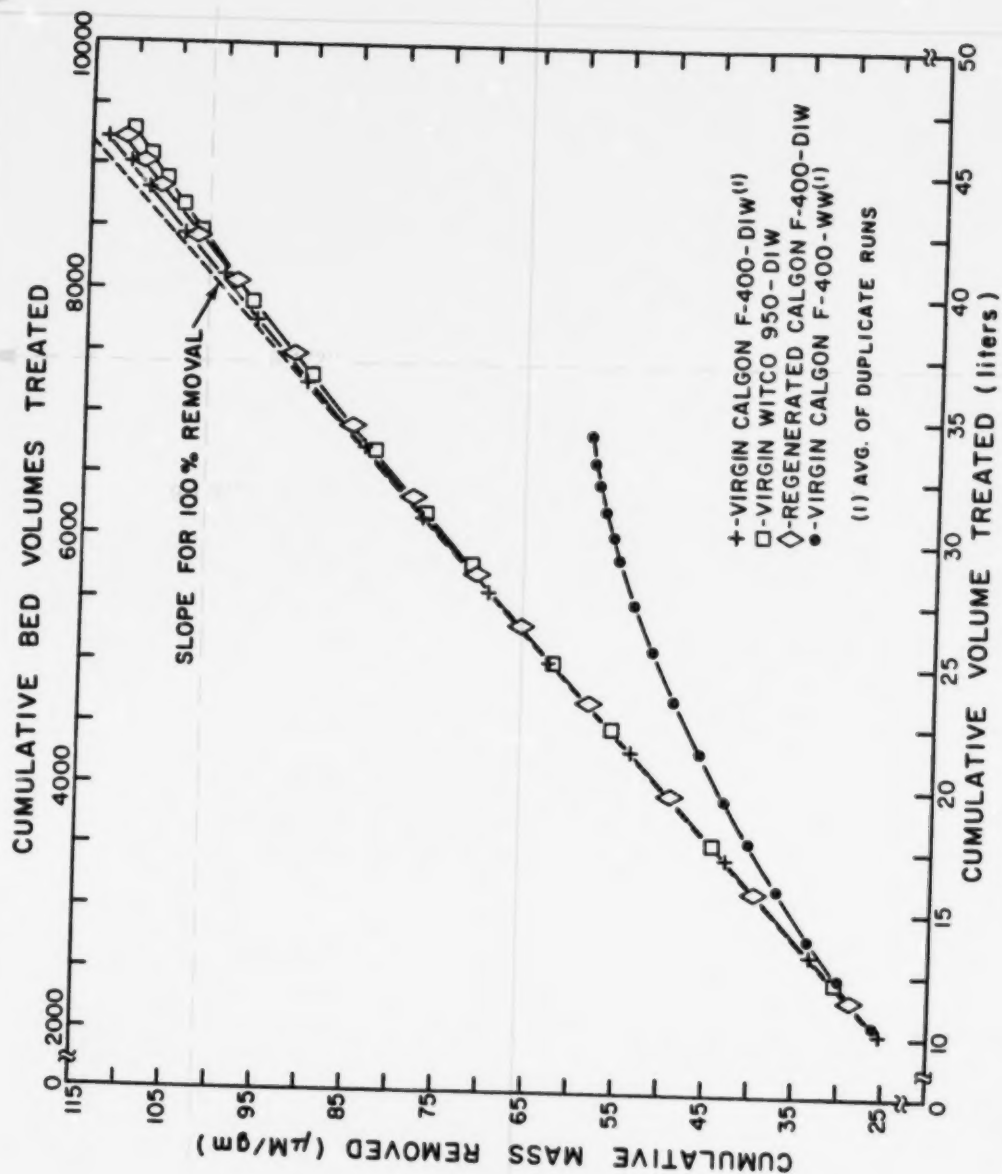


Figure 20. Breakthrough curves for 2-Chlorophenol.

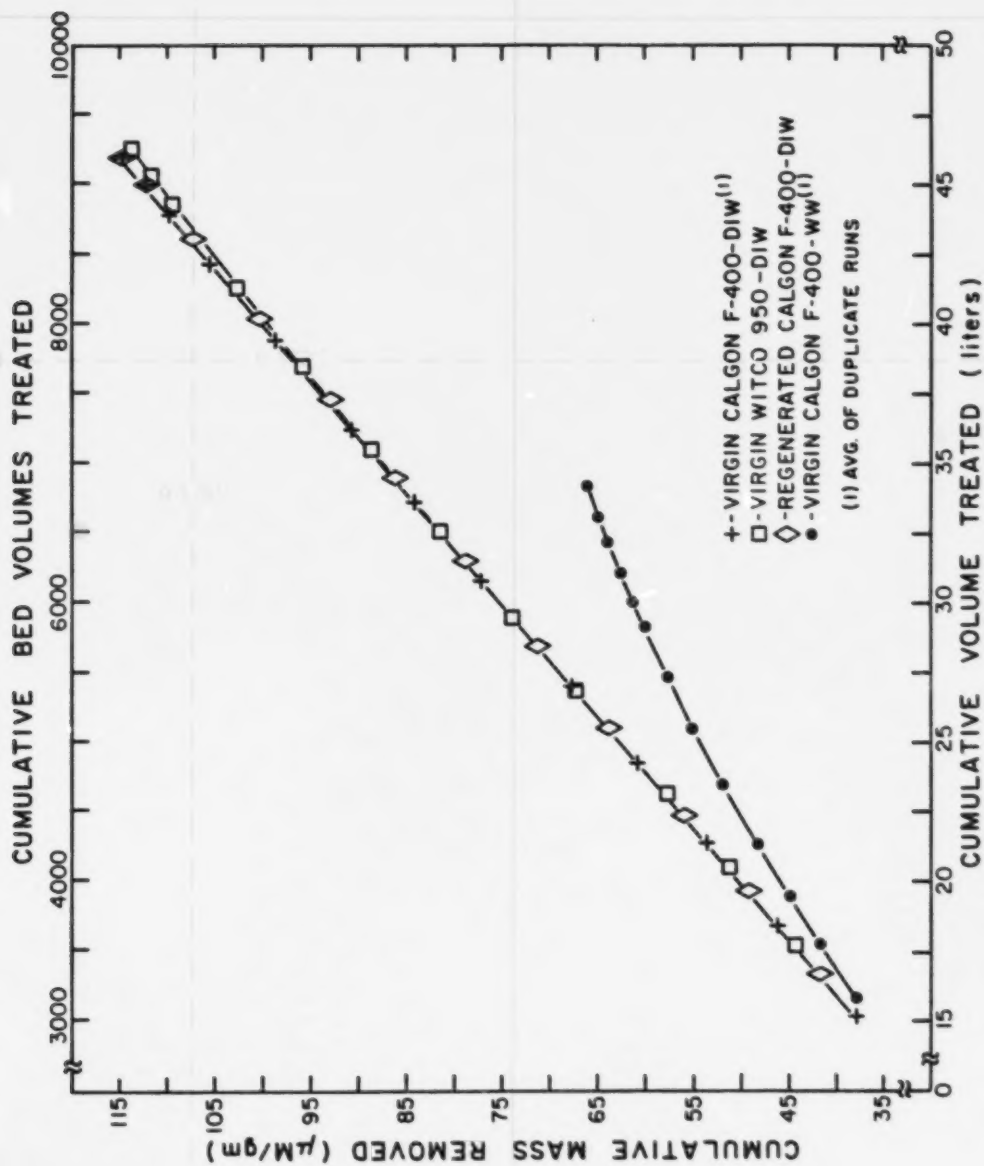


Figure 21. Breakthrough curves for 2,4 Dimethylphenol.

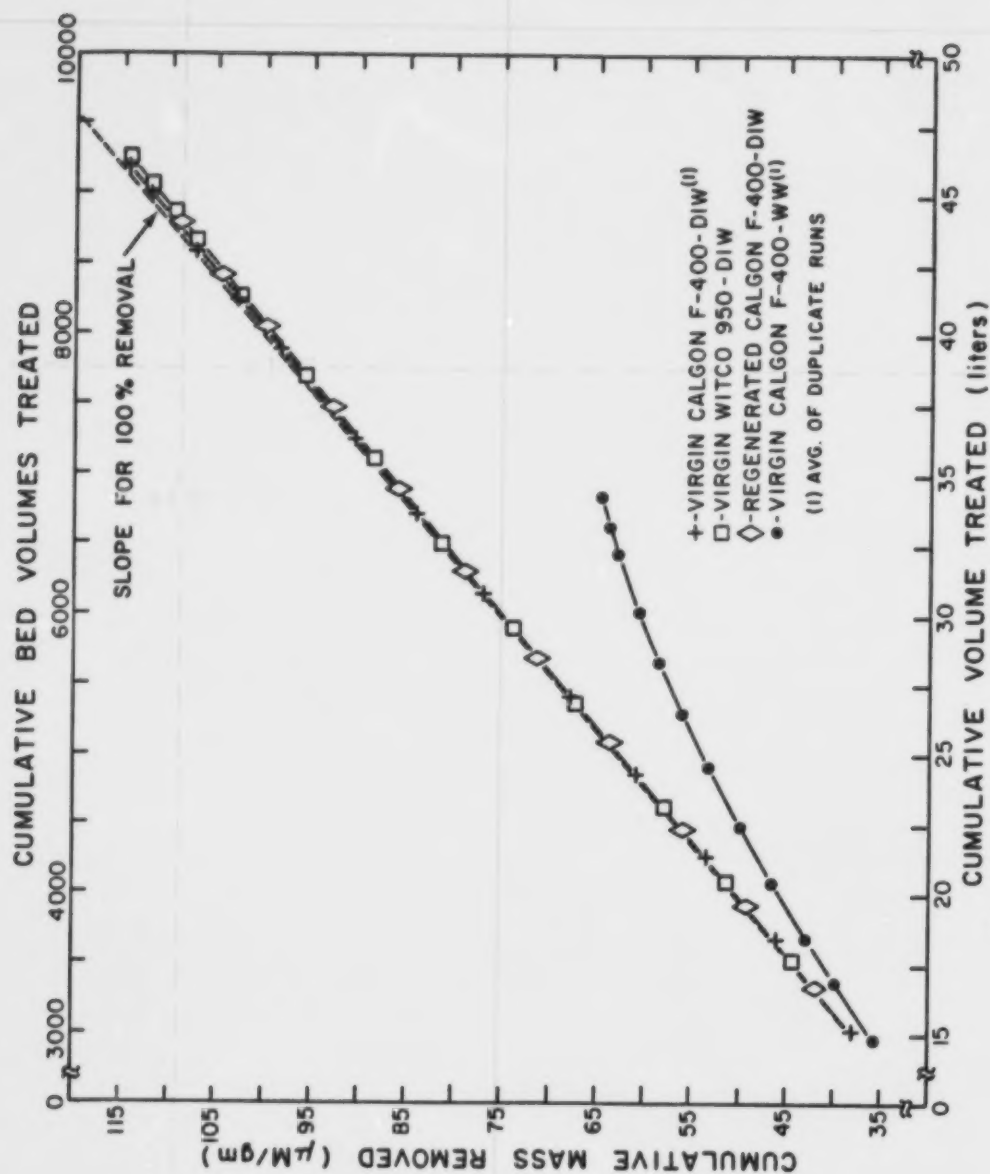


Figure 22. Breakthrough curves for 2,4-Dichlorophenol.

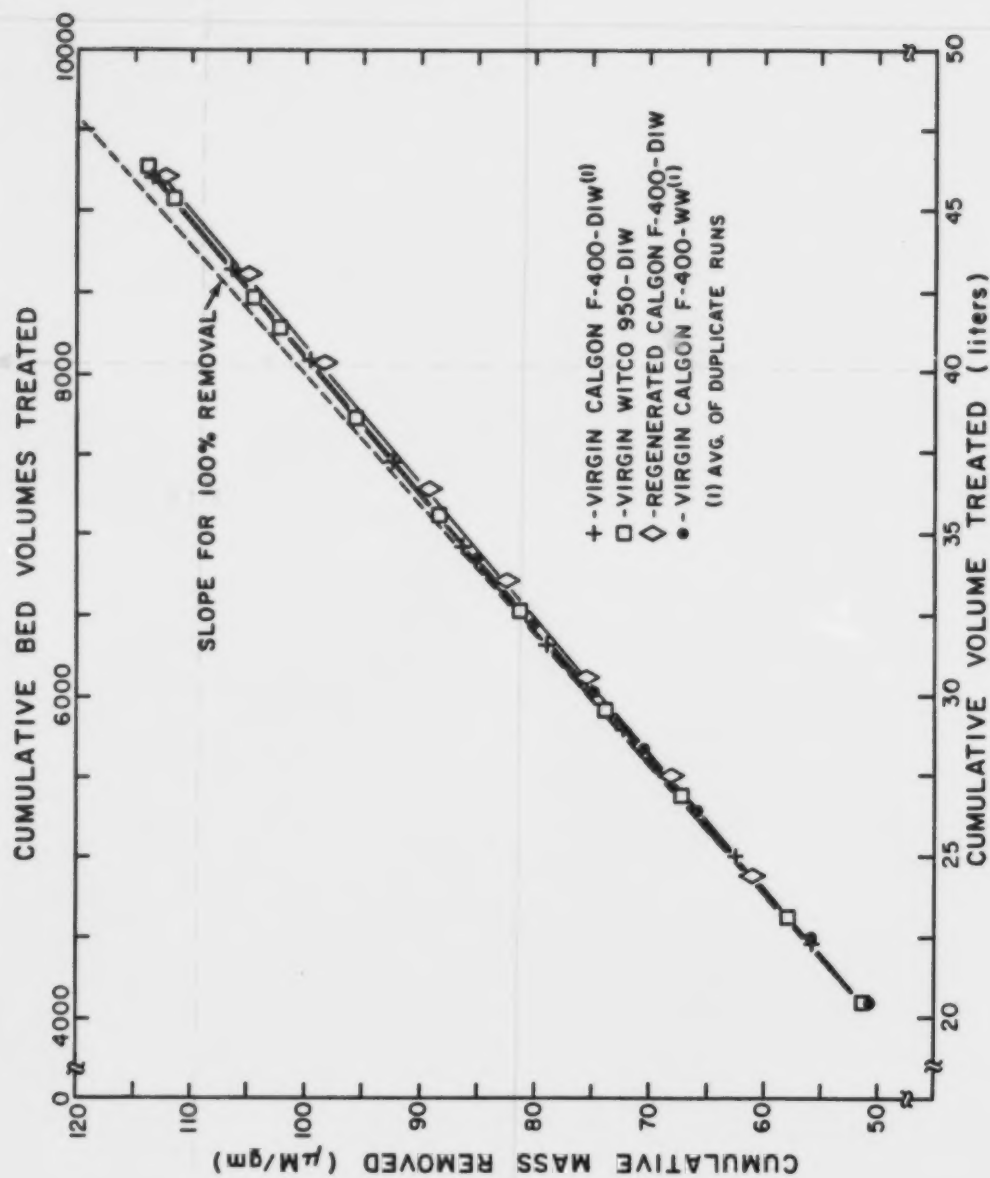


Figure 23. Breakthrough curves for Dimethyl Phthalate.

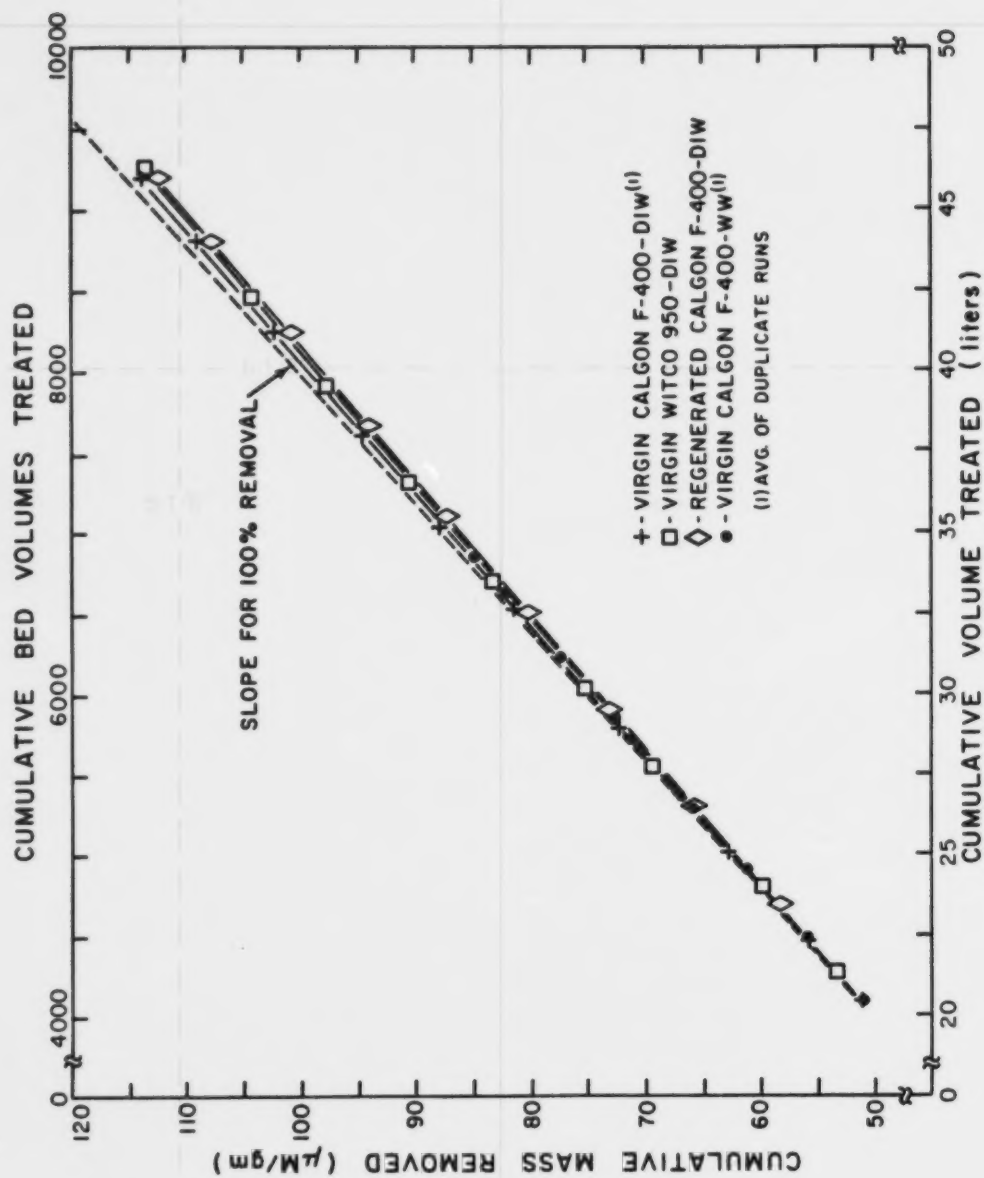


Figure 24. Breakthrough curves for Diethyl Phthalate.

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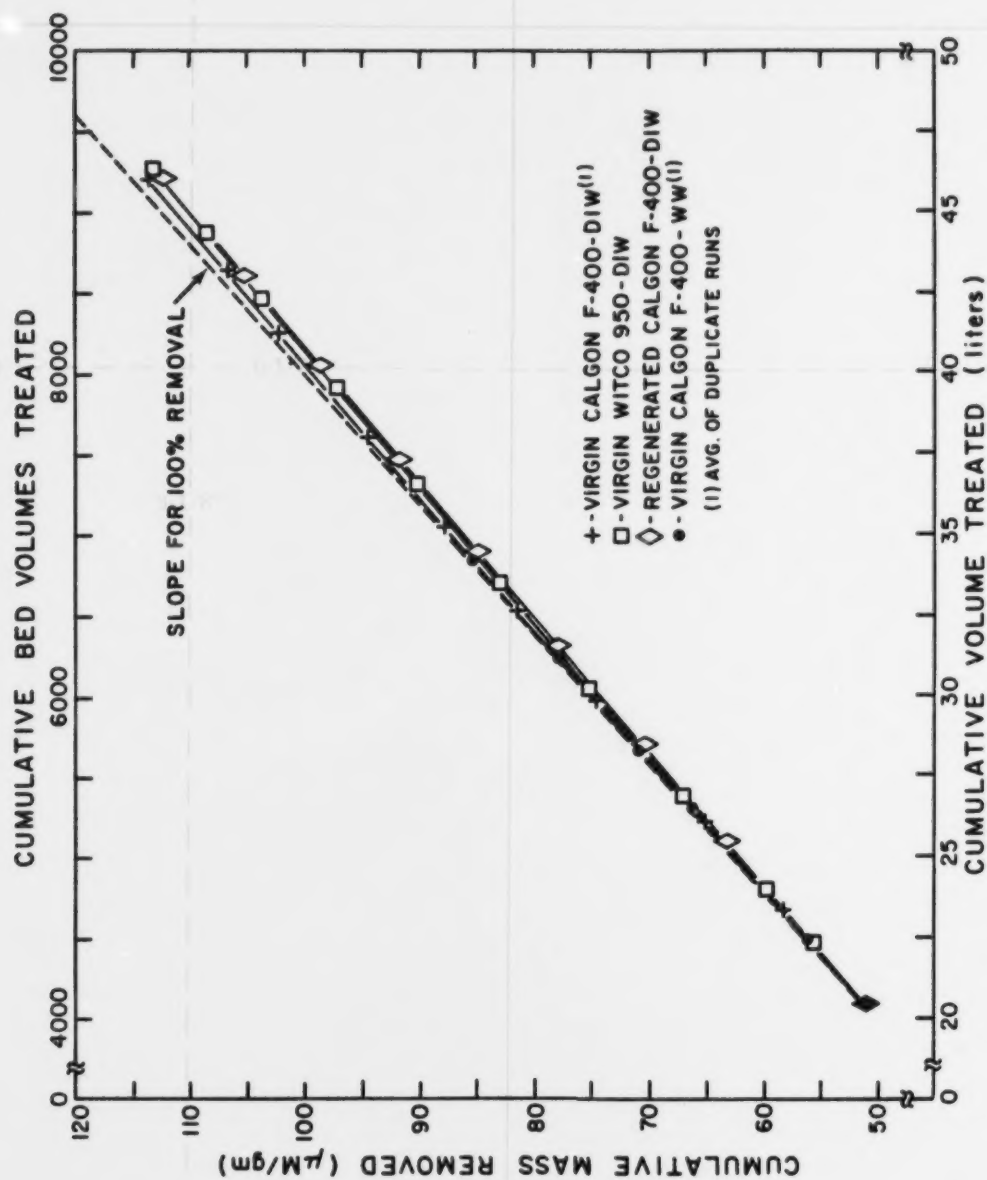


Figure 25. Breakthrough curves for Di-N-Butyl Phthalate .

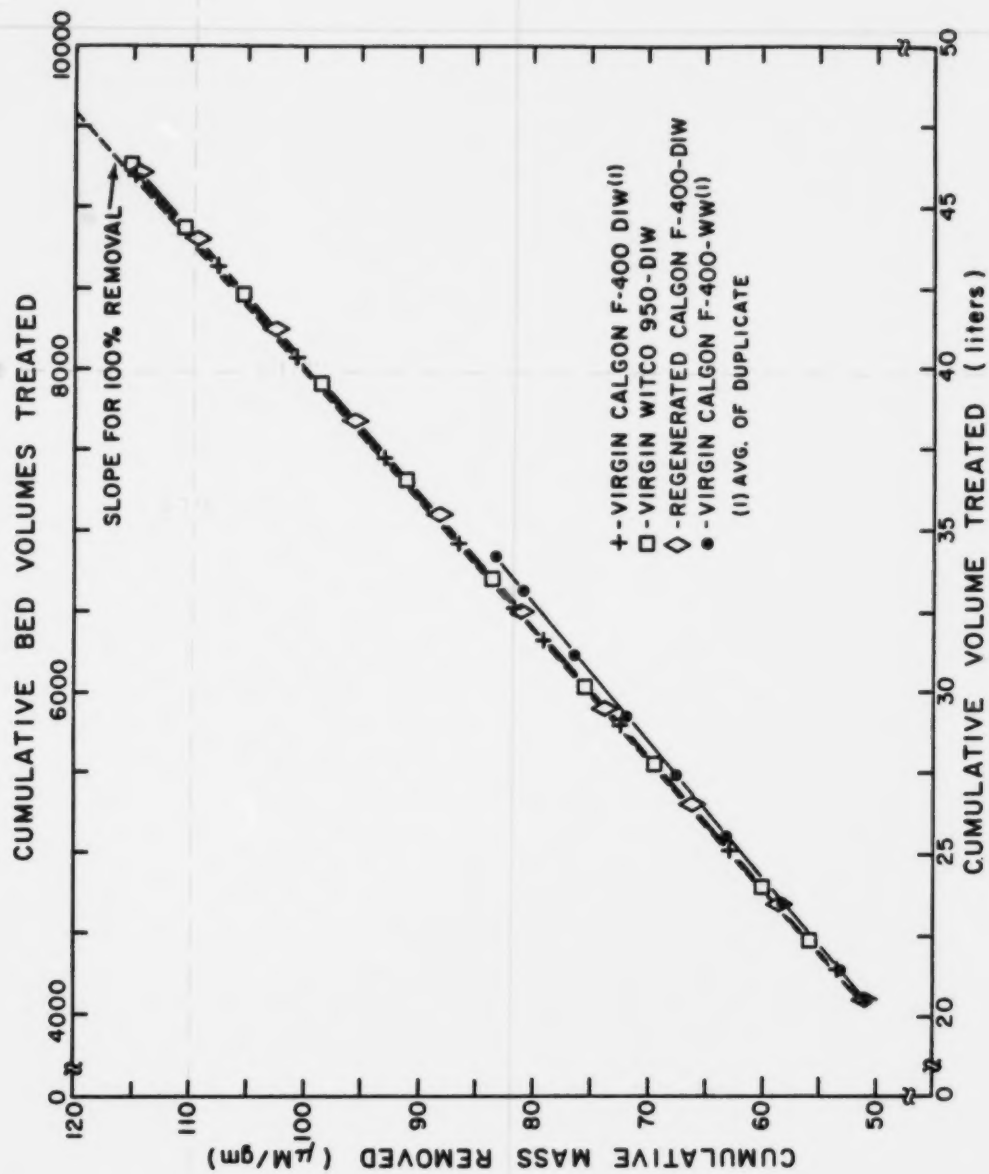


Figure 26. Breakthrough curves for Acenaphthylene.

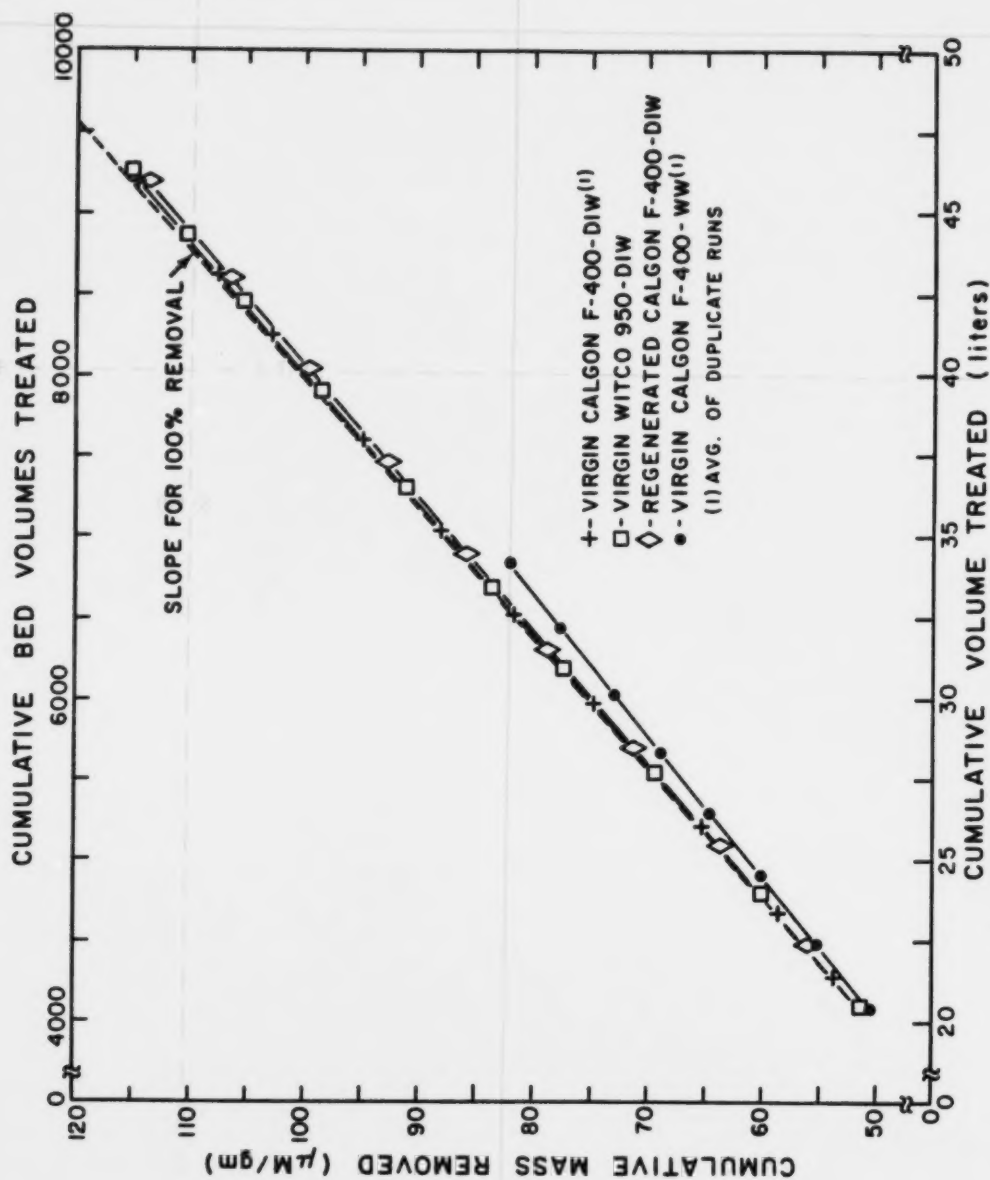


Figure 27. Breakthrough curves for 1,4 Dichlorobenzene.

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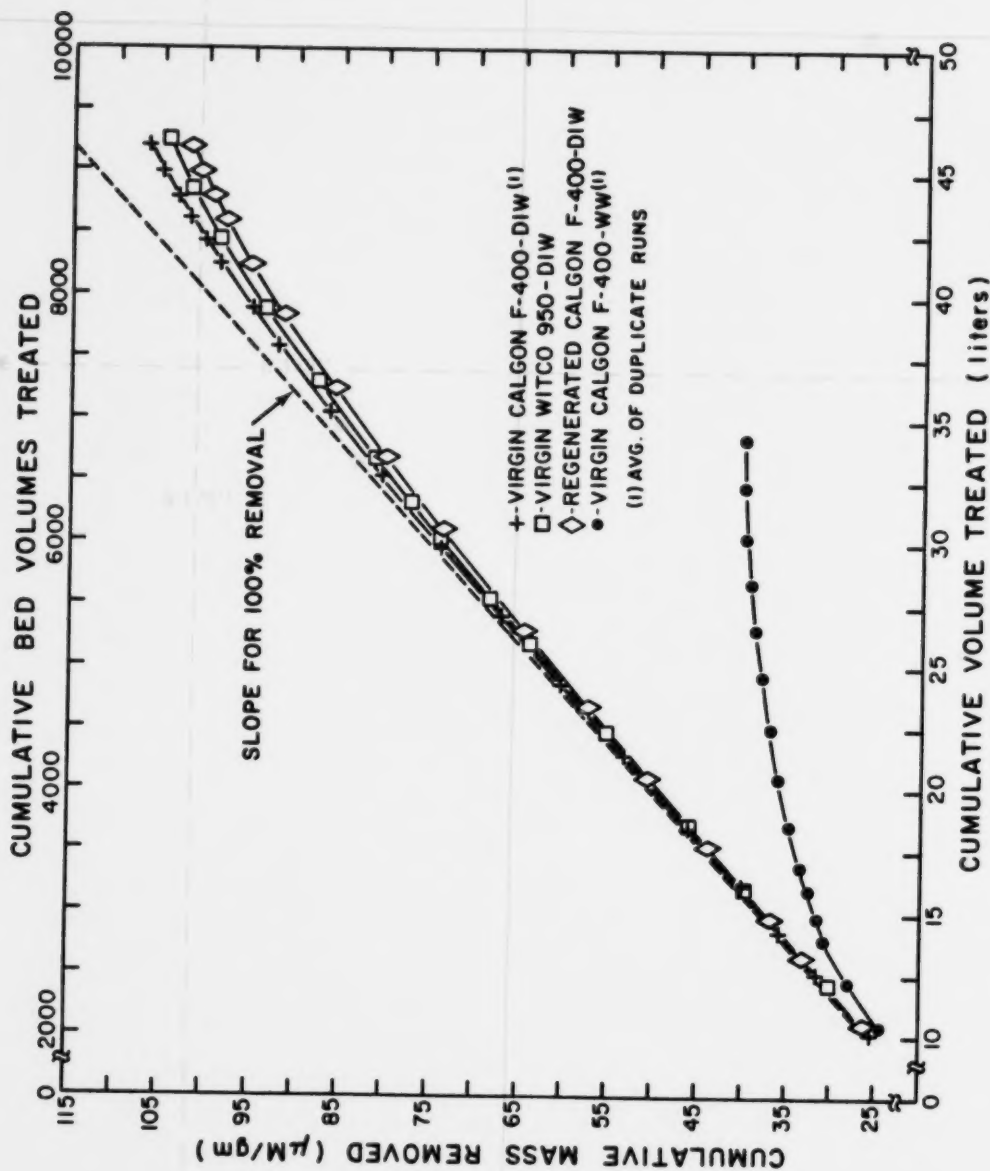


Figure 28. Breakthrough curves for 1,1,2,2-Tetrachloroethane .

TABLE 39. REPRODUCIBILITY OF BREAKTHROUGH CHARACTERISTICS FROM ELEVEN COMPONENT DIW MATRIX

Component	Initial BP (1)		~10% BP (2)		% BT		Run Termination (3)	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Cum. Capacity	Run 1
Phenol	3875	4229	6299(78.25)	6305(78.40)	91.2	112.6	112.19	111.00
2-nitrophenol	4661	4408	7223(89.81)	7167(89.15)	49.5	53.3	122.93	122.41
2-chlorophenol	4847	4966	9181(112.98)	8865(109.26)	19.8	24.5	129.95	129.93
2,4-dimethylphenol	6299	6460	-----	-----	1.9	2.8	135.08	135.32
2,4-dichlorophenol	6299	6305	-----	-----	3.6	5.3	134.25	134.64
Dimethyl Phthalate	2370	2408	-----	-----	7.6	7.9	132.42	132.96
Diethyl Phthalate	2370	2408	-----	-----	7.3	7.9	133.00	133.40
Di-n-butyl Phthalate	2195	2408	-----	-----	6.9	7.2	132.88	133.41
Acenaphthylene	6139	6305	-----	10643(133.07)	8.9	10.3	134.98	135.63
1,4-dichlorobenzene	5769	5753	-----	-----	3.5	4.2	134.12	134.70
1,1,2,2-tetrachloroethane	1044	1105	6894(84.69)	7038(86.24)	63.1	64.8	115.67	115.55

- (1) Initial breakpoint in bed volumes treated.
 (2) Breakpoint indicated in bed volumes treated with cumulative carbon capacity given in $\mu\text{M/gm}$ in parenthesis.
 (3) For comparative purposes, 10807 bed volumes were used as Run 1 termination. Actual run termination was 11006 bed volumes. Run 2 was terminated at 10850 bed volumes treated. Cumulative carbon capacity in $\mu\text{M/gm}$.

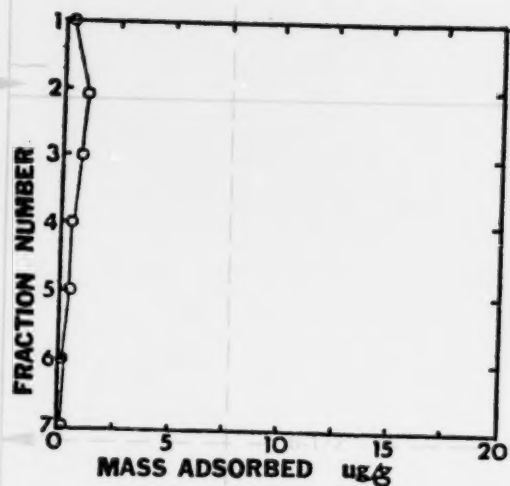
TABLE 40. REPRODUCIBILITY OF BREAKTHROUGH CHARACTERISTICS FROM ELEVEN-COMPONENT WASTEWATER MATRIX

Component	Initial Bp ⁽¹⁾		~10% Bp ⁽²⁾		~50% Bp ⁽²⁾		% BT		Run Termination ⁽³⁾	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Phenol	765	711	---	---	---	---	1.3	<1	84.84	83.24
2-nitrophenol	365	508	1900(23.08)	1815(22.06)	2604(29.02)	2544(28.20)	156	141	21.01	21.45
2-chlorophenol	976	1064	2604(31.84)	2544(31.13)	4900(50.21)	5008(51.05)	81.2	77.4	58.69	58.72
2,4-dimethylphenol	976	1064	2783(33.92)	2735(33.73)	6215(62.33)	6355(64.05)	61.1	55.8	65.70	66.02
2,4-dichlorophenol	1161	1064	2783(33.65)	2544(31.10)	5651(58.42)	5578(58.08)	66.5	61.6	64.60	64.47
Dimethyl Phthalate	765	711	---	---	---	---	1.2	1.4	84.97	83.01
Diethyl Phthalate	365	339	---	---	---	---	2.0	1.0	84.77	83.04
Di-n-butyl Phthalate	365	339	---	---	---	---	<1	<1	85.33	83.74
Acenaphthylene	2086	2195	---	---	---	---	8.3	7.8	83.32	81.97
1,4-dichlorobenzene	1717	1815	6422(77.47)	6693(80.83)	---	---	12.4	11.1	81.90	80.83
1,1,2,2-tetrachloroethane	191	339	1717(20.61)	1635(19.83)	2964(31.48)	2735(29.42)	100.8	99.4	40.00	39.59

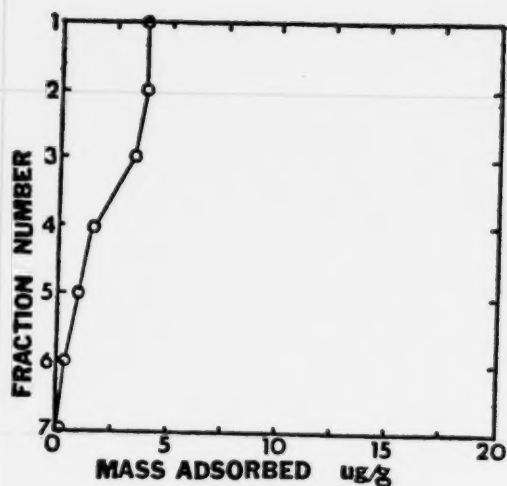
(1) Initial breakthrough in bed volumes treated.

(2) Breakpoint indicated in bed volumes treated with cumulative carbon capacity in $\mu\text{M/gm}$ given in parenthesis.

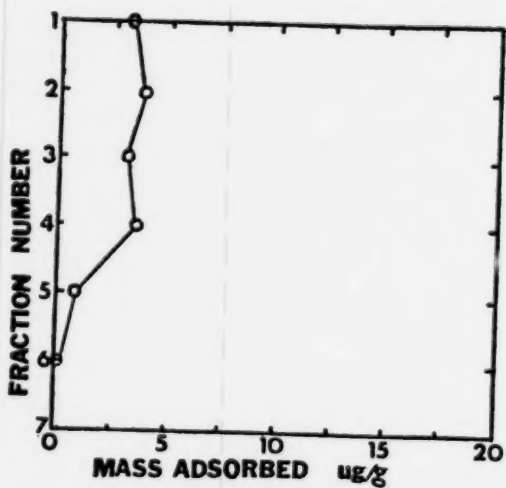
(3) Run 1 terminated at 6823 bed volumes treated and Run 2 terminated at 6693 bed volumes treated.



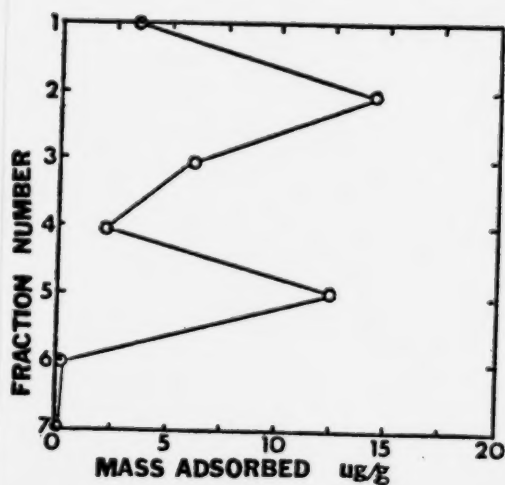
A) 2-CHLOROPHENOL



B) PHENOL

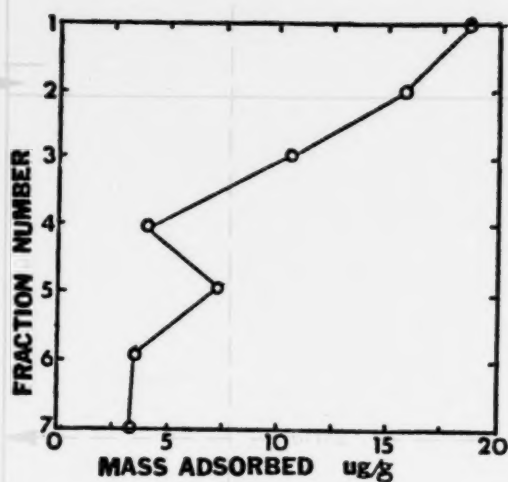


C) 2-NITROPHENOL

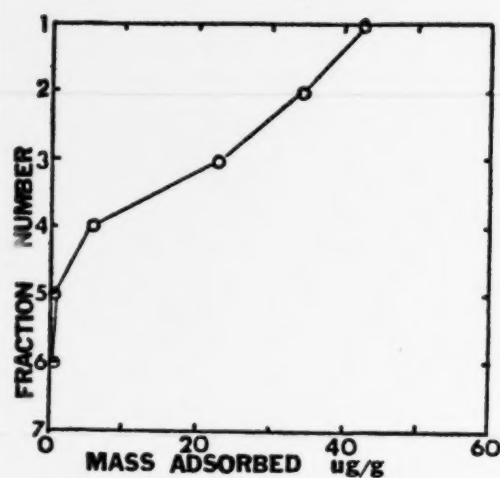


D) 2,4-DIMETHYLPHENOL

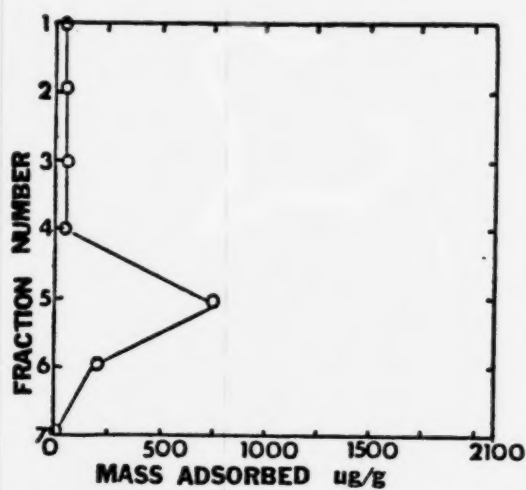
FIGURE 29. TOXICANT MOVEMENT WITHIN THE CARBON COLUMN (5-29-80 SITE STUDY).



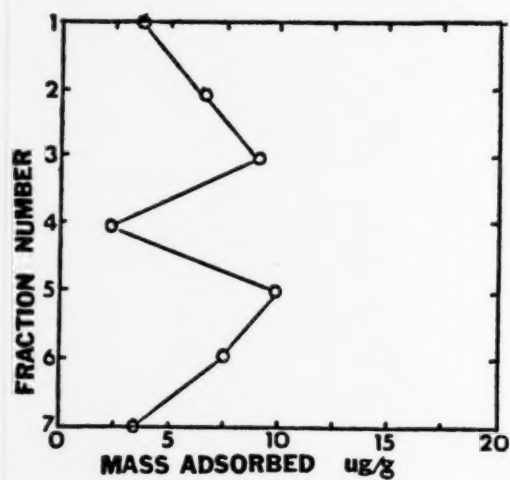
E) 2,4-DICHLOROPHENOL



F) 2,4,6-TRICHLOROPHENOL

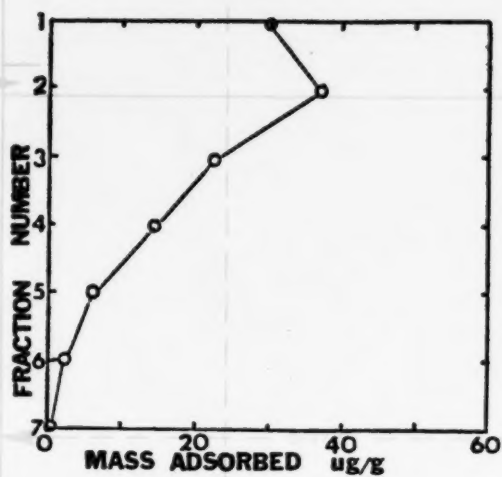


G) 4,6-DINITRO-O-CRESOL

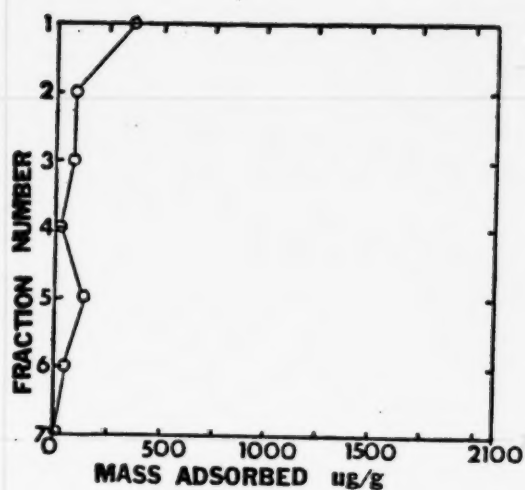


H) 1,4-DICHLOROBENZENE

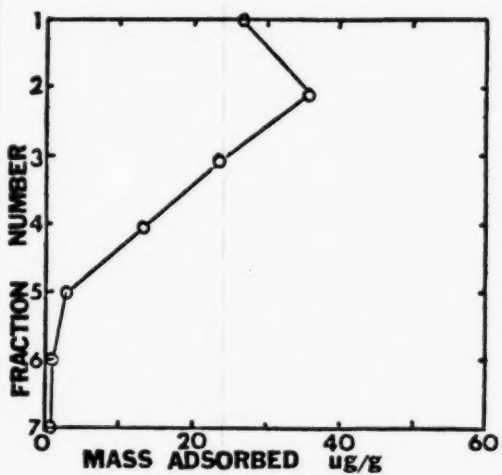
FIGURE 29 (CONTINUED)



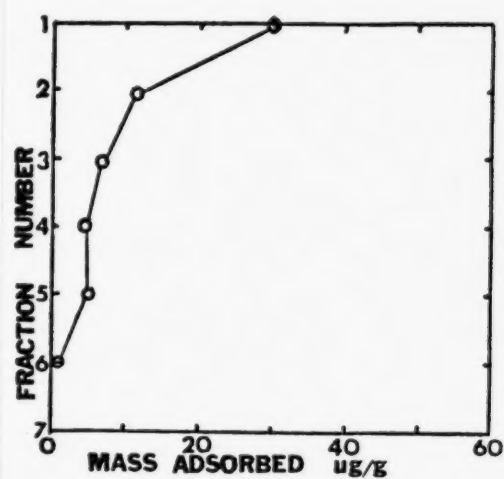
I) DIMETHYL PHTHALATE



J) DIETHYL PHTHALATE

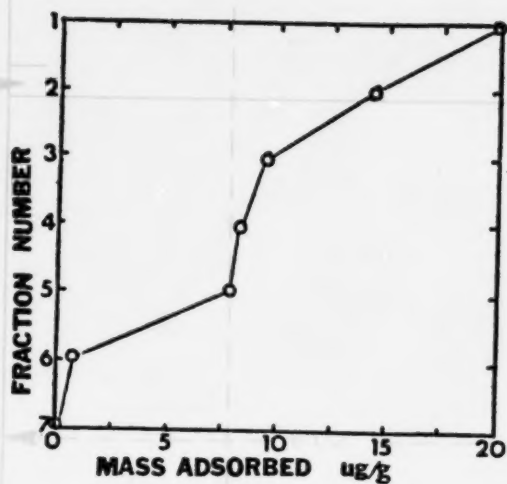


K) DI-N-BUTYL PHTHALATE

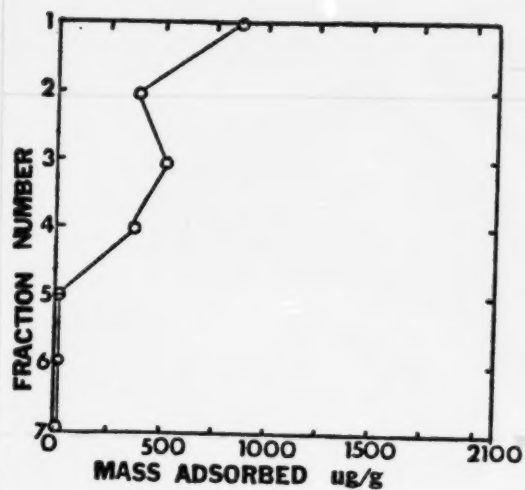


L) ACENAPHTHYLENE

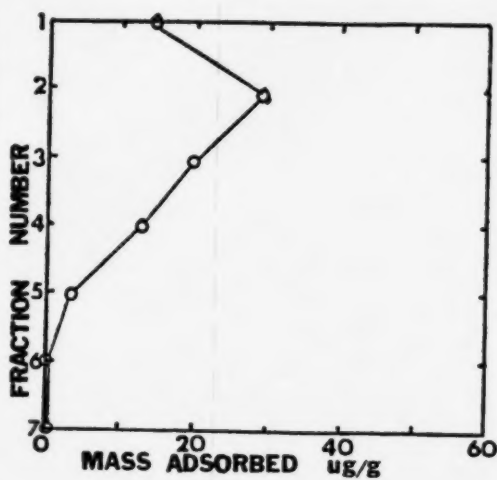
FIGURE 29 (CONTINUED)



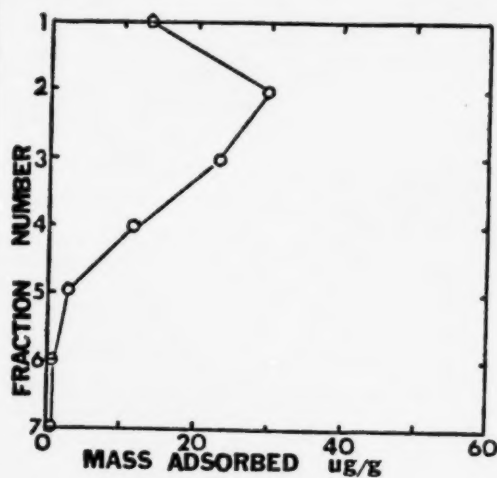
M) ACENAPHTHENE



N) FLUORENE



O) PHENANTHRENE



P) ANTHRACENE

FIGURE 29 (CONTINUED)

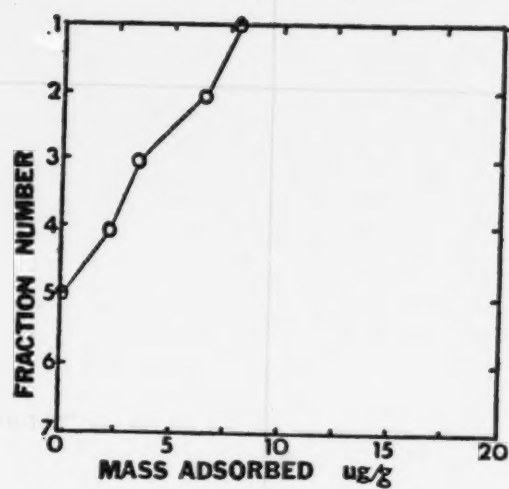


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Analysis of toxicant movement within the carbon column was also performed on the carbon column used in the 4-81 site study conducted in the laboratory. Data pertinent to these analyses are presented in Table 42, and results are presented graphically (as described for the 5-80 site study) in Figure 30.

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TABLE 42. CARBON COLUMN EXTRACTION DATA FOR THE 4-81 SITE STUDY

Fraction No. (1)	Approximate Section Thickness(cm)	Mass of Carbon In Section(g)	Mass of Carbon Extracted(g)
1	5	32.6	32.6
2	5	36.9	36.9
3	5	36.3	36.3
4	5	40.7	40.7
5	5	32.1	32.1
6	5	38.9	38.9

- (1) Fraction 1 is from the top (influent) end of the carbon column, and fraction 6 is from the bottom (effluent) end.

Breakthrough of several study toxicants occurred within the duration of the longer 4-81 site study (680 bed volumes treated). Liquid-liquid extraction data is used for the presentation of effluent toxicant data because detection sensitivity proved comparable to XAD resin extraction techniques, and approximate recovery efficiencies had been determined for the liquid-liquid extraction procedure. Results of carbon column effluent analyses for specific toxicants are illustrated graphically in Figure 31, and presented quantitatively in Table 43.

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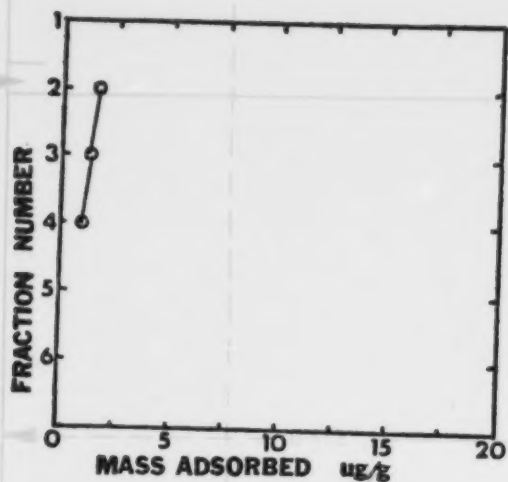
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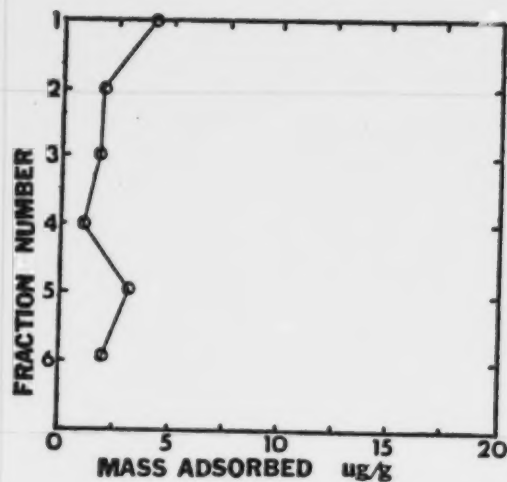
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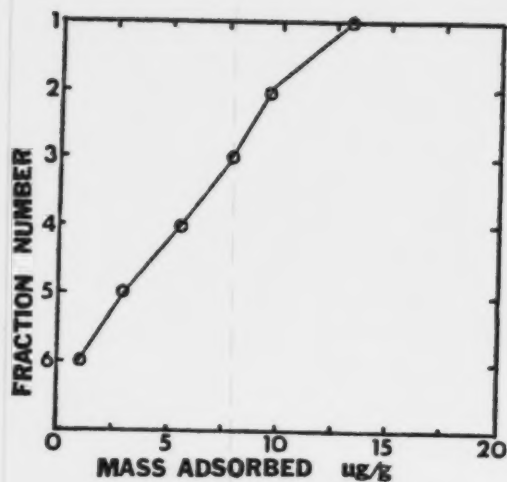
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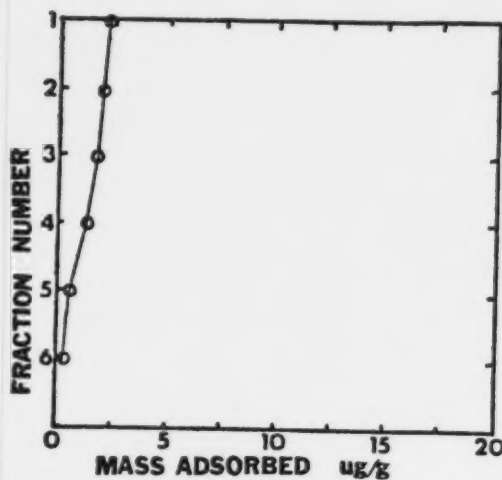
A) 2-CHLOROPHENOL



B) PHENOL



C) 2-NITROPHENOL



D) 2,4-DIMETHYLPHENOL

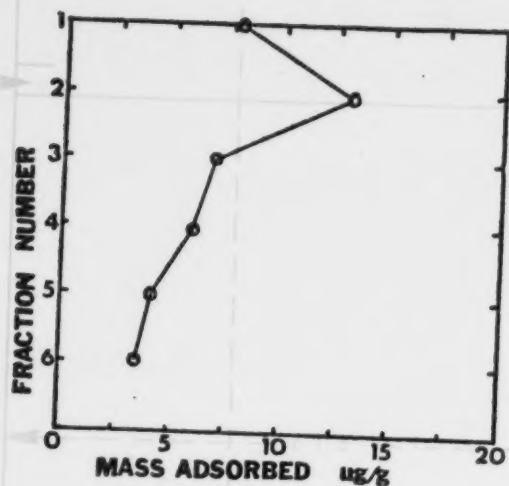
FIGURE 30. TOXICANT MOVEMENT WITHIN THE CARBON COLUMN (4-22-81 SITE STUDY).

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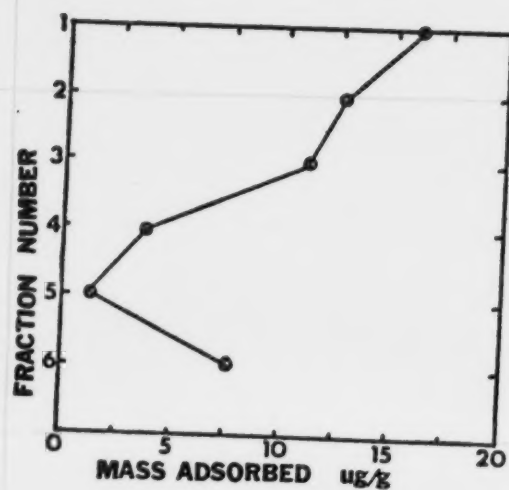
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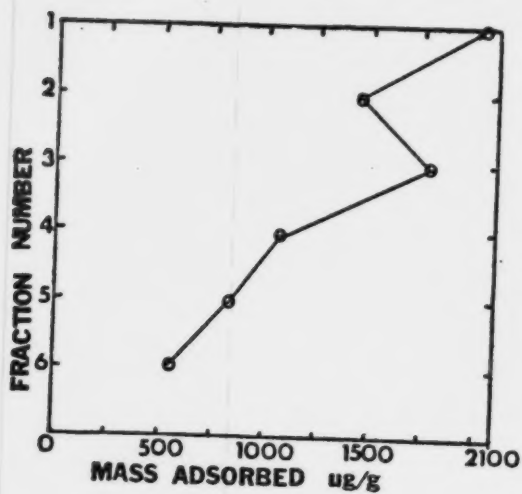
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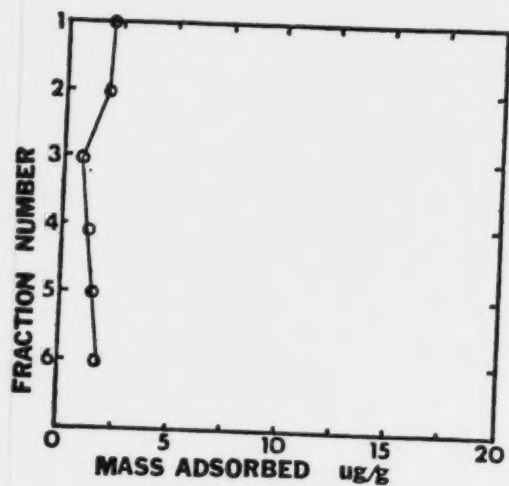
E) 2,4-DICHLOROPHENOL



F) 2,4,6-TRICHLOROPHENOL



G) 4,6-DINITRO-O-CRESOL



H) 1,4-DICHLOROBENZENE

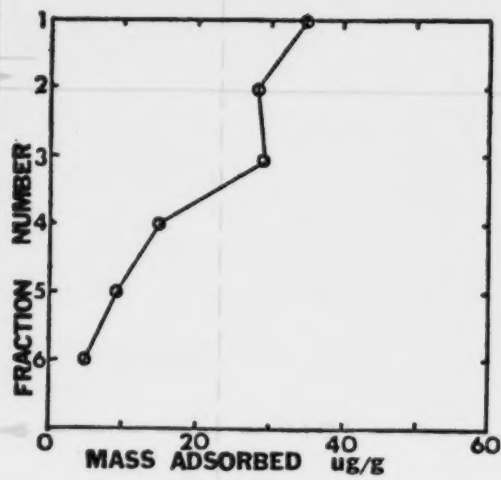
FIGURE 30 (CONTINUED)

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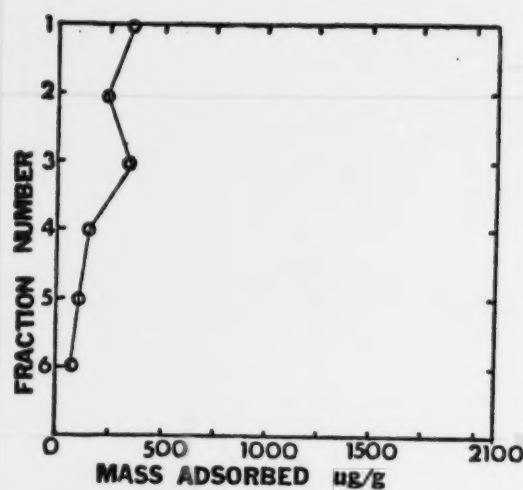
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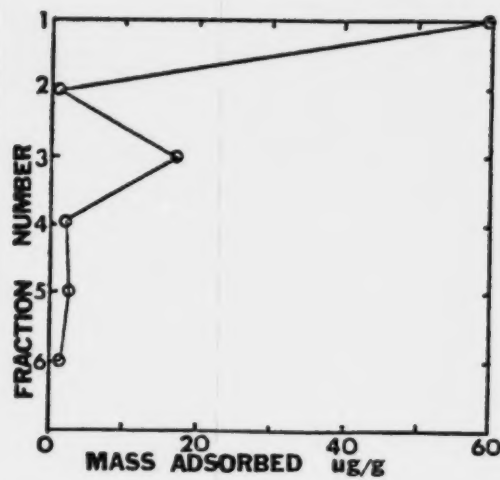
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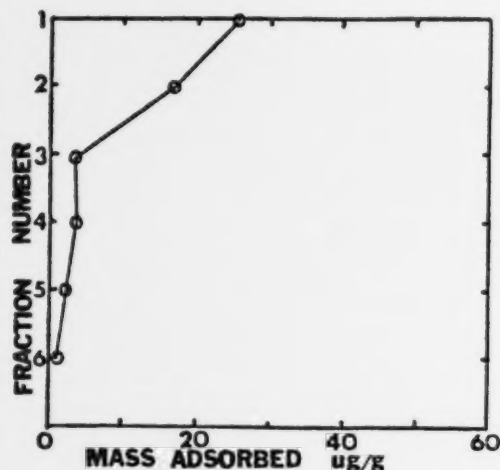
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J) DIETHYL PHTHALATE



K) DI-N-BUTYL PHTHALATE



L) ACENAPHTHYLENE

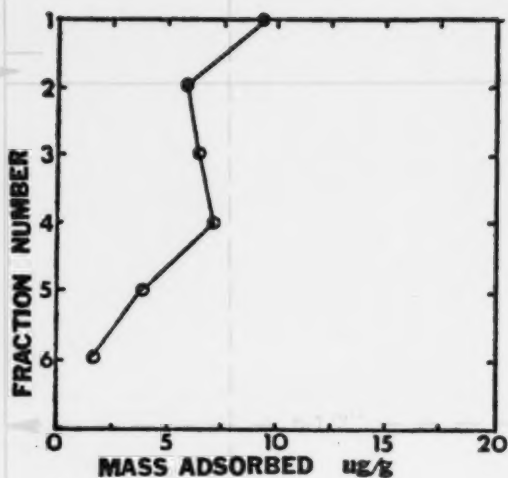
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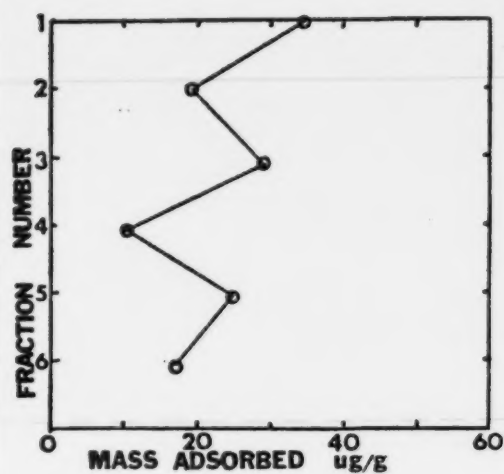
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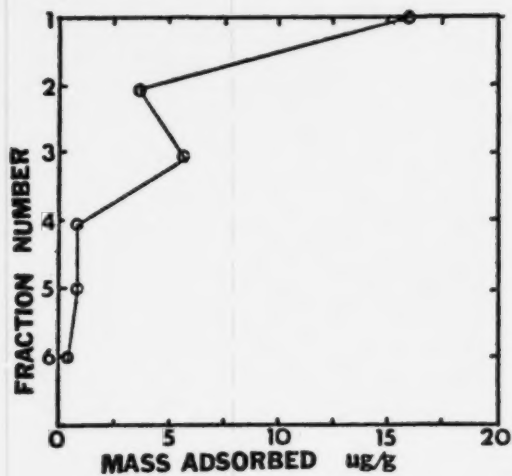
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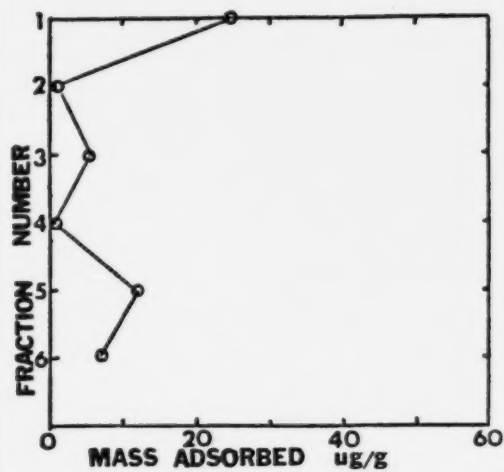
M) ACENAPHTHENE



N) FLUORENE



O) PHENANTHRENE



P) ANTHRACENE

FIGURE 30 (CONTINUED)

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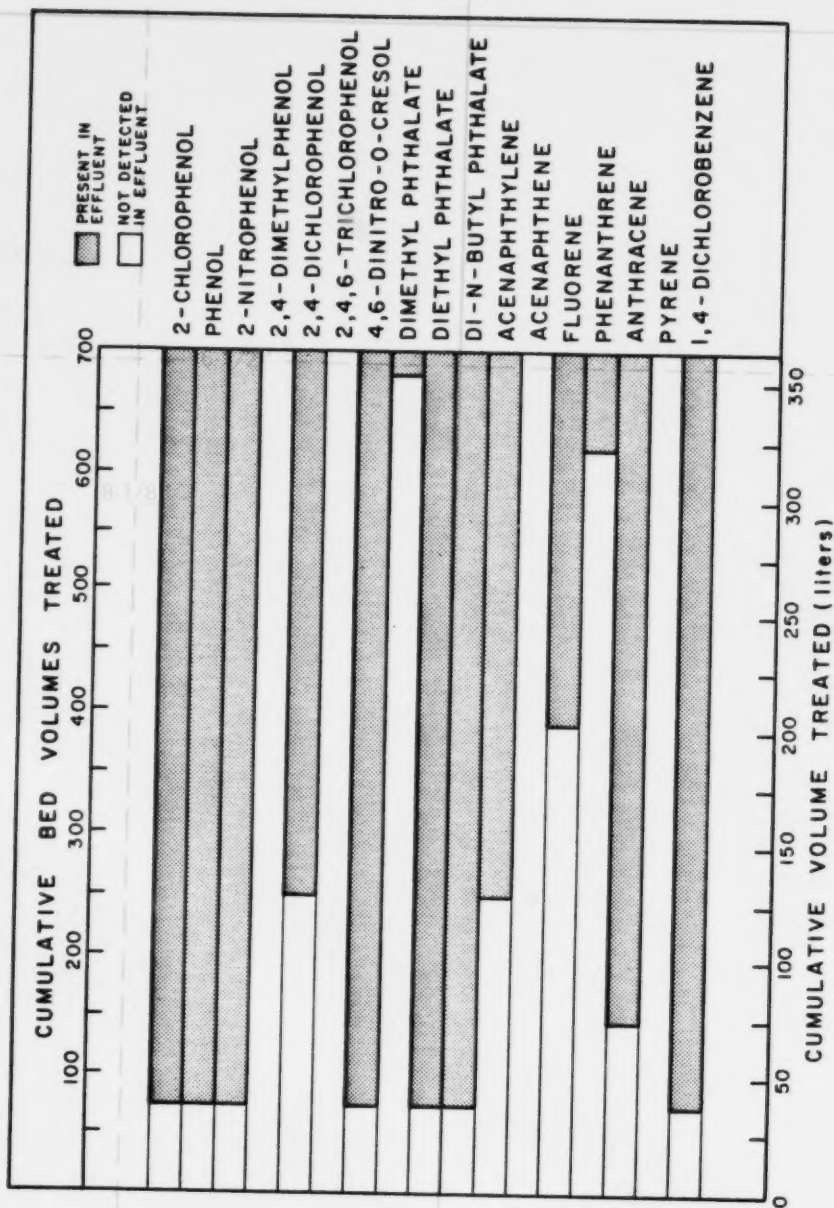


Figure 31. Column effluent profile from 4-22-81 site study (LLE Data)

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TABLE 43. CARBON COLUMN EFFLUENT TOXICANT LEVELS FOR 4-81 SITE STUDY (1)

Compound	Toxicant Effluent Level ($\mu\text{g/l}$) At Point Indicated (In Bed Volumes Treated)									
	1.9	73.1	144.2	250.0	321.2	392.3	434.6	525.0	623.1	682.7
2-chlorophenol	ND ⁽²⁾	<0.5	0.64	0.66	<0.5	0.92	1.26	0.56	<0.5	<0.5
Phenol	ND	0.73	0.82	0.63	0.88	0.84	0.85	<0.5	<0.5	<0.5
2-nitrophenol	ND	<0.9	0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9
2,4-dimethylphenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-dichlorophenol	ND	ND	ND	<0.8	<0.8	<0.3	<0.8	<0.8	<0.8	<0.8
2,4,6-trichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4,6-dinitro-o-cresol(*)	ND	20.4	76.4	106	120	7.50	138	295	299	251
Dimethyl Phthalate	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.99
Diethyl Phthalate(*)	ND	2.97	5.26	1.62	<0.9	<0.9	<0.9	1.23	1.04	3.49
Di-n-butyl Phthalate(*)	ND	3.51	8.15	4.15	0.98	<0.9	<0.9	5.68	<0.9	3.18
Acenaphthylene	ND	<0.9	<0.9	<0.9	<0.9	0.9	1.98	<0.9	<0.9	1.30
Acenaphthene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluorene	ND	ND	ND	ND	ND	3.90	<0.8	<0.8	<0.8	<0.8
Phenanthrene	ND	ND	ND	ND	ND	ND	ND	ND	<1.0	<1.0
Anthracene(*)	ND	ND	9.48	3.07	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,4-dichlorobenzene(*)	ND	<0.9	<0.9	1.11	<0.9	0.92	<0.9	<0.9	<0.9	<0.9

(1) Refer to Table 32 for column influent concentration levels.

(2) ND = none detected.

(*) Presence verified by mass spectrometry in effluent fraction #3 (144.2 bed volumes).

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SECTION 8

DISCUSSION

SINGLE SOLUTE STUDIES

Adsorptive capacities established in single solute DIW matrices represent maximum values for the experimental conditions used, since no other species are present to compete for adsorption sites in these systems. For a given set of adsorption conditions (column dimensions, carbon particle size, EBCT, etc.) adsorptive capacity for a particular compound is dependent upon influent concentration, particularly in the absence of competing species. The concentration capacity relationship is one of increasing adsorbent capacity as influent concentration increases. The data obtained for adsorption of phenol (Figure 3) indicate that this relationship is log-log linear, at least for simple matrices. These observations are consistent with findings of Weber and Keinath (1967) for GAC adsorption of sulfonated alkylbenzene. Working with single solute, continuous-flow systems, they found both the rate of mass transfer and carbon capacity for sulfonated alkylbenzene to increase linearly with increasing influent concentration.

The increase in carbon capacity likely results from enhanced adsorption within the internal pore structure of the carbon particles. Greater solution concentration establishes a stronger driving force for mass transfer of solute molecules across the solvent-solid interface. As a result, the surfaces of adsorbent particles become saturated more rapidly, and film diffusion is rate limiting for a shorter period of time (Weber and Keinath, 1967). At this point, intraparticle transport becomes the rate limiting step in the adsorption process, and adsorption within the pore structure becomes significant. Saturation of the particle surface with adsorbate molecules creates a concentration gradient which makes intraparticle transport more favorable, resulting in enhanced adsorption within the pore structure. Thus, as previously adsorbed molecules are transported to internal adsorption sites surface sites are freed for continued solute removal, and adsorptive capacity is increased.

Solute concentration is an extremely important consideration in GAC column treatment applications, because it has a direct effect on adsorptive capacity and greatly influences competitive adsorption phenomena. The absolute concentration of individual solutes, and the relative concentration of competing species, are primary factors controlling GAC removal efficiency in complex matrices. Removal efficiency and carbon

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capacity in turn determine initial GAC requirements and carbon regeneration frequency, which dictate the costs of treatment.

Single solute adsorption studies were run at equimolar concentration levels (with the exception of acenaphthylene, due to aqueous solubility limitations) because of the concentration-capacity dependence. The equimolar approach was selected because the objective was to formulate adsorption matrices containing equal numbers of adsorbate molecules, rather than equal masses. Thus by normalizing the concentration influence, results obtained from these investigations provided a comparable measure of the intensity of adsorbate-adsorbent affinities. Carbon capacity measurements from these studies provided: 1) a means for comparison of continuous-flow and batch adsorption data; 2) a means for evaluation of adsorbate characteristics potentially useful for predicting amenability to GAC adsorption; and, 3) a criterion for prediction of solute behavior in more complex adsorption matrices.

For the components used in single solute adsorption systems, carbon capacity decreased according to the following general pattern; PNA's > chlorinated hydrocarbons > phthalate esters > phenols. Adsorption patterns observed in these investigations were compared with adsorbate characteristics and literature batch adsorption parameters for each compound to determine if useful correlations existed. A comparison of adsorption data from batch and experimental column systems is summarized in Table 44.

TABLE 44. ADSORPTION CHARACTERISTICS FROM BATCH AND CONTINUOUS-FLOW SYSTEMS

Compound	Batch System ⁽¹⁾		Continuous-flow System	
	Capacity ⁽²⁾	Slope ⁽³⁾	Capacity ⁽⁴⁾	Initial BP ⁽⁵⁾
Phenol	21	0.54	112	2785
2,4-dimethylphenol	73	0.44	321	3713
Dimethyl Phthalate	97	0.41	314	4841
Diethyl Phthalate	110	0.27	431	5283
Acenaphthylene	115	0.37	>>140	3550
1,4-dichlorobenzene	121	0.47	>662	6739

- (1) Data from Dobbs and Cohen (1980).
- (2) Carbon capacity in mg/l from Freundlich equation isotherm for an equilibrium concentration of 1 mg/l at neutral pH.
- (3) Slope of the Freundlich equation isotherm.
- (4) Carbon capacity in mg/g-carbon.
- (5) Initial breakpoint in bed volumes treated.

Comparison of adsorptive phenomena observed in these studies with batch adsorption parameters is of particular interest because batch data is frequently used for prediction of column performance. Comparison of absolute capacity data was not possible because initial adsorbate concentrations used in batch systems were either different or not given, so a rela-

tive basis was examined. Relative carbon affinities, as indicated by adsorptive capacity, established in continuous-flow systems closely followed literature data from batch studies. A reversal in the position of 2,4-dimethylphenol and dimethyl phthalate was the only inconsistency observed between these data, and this was of dubious significance because of the minimal capacity differences.

Two thermodynamically related adsorbate characteristics, aqueous solubility and n-octanol/water partition coefficients, were selected for comparison with the data obtained from single-solute adsorption experiments. Adsorbate classification based on either parameter has a thermodynamic basis and thus should be of general applicability. Both adsorbate characteristics have been suggested to be useful criteria for predicting solute amenability to sorption processes (Karickhoff et al., 1979). A comparison of these two adsorbate parameters with adsorption data obtained in this study is given in Table 45.

TABLE 45. RELATIONSHIP BETWEEN ADSORBATE PARAMETERS AND EXPERIMENTAL ADSORPTION DATA

Compound	Continuous-flow System		Aqueous Solubility ⁽³⁾	Log K _{ow} ⁽⁴⁾
	Capacity ⁽¹⁾	Initial BP ⁽²⁾		
Phenol	112	2785	93000	1.48(USEPA,1980(a))
2,4-dimethylphenol	321	3713	4700	3.62(USEPA,1980(b))
Dimethyl Phthalate	314	4841	4000	3.13(USEPA,1980(c))
Diethyl Phthalate	431	5283	1000	3.49(USEPA,1980(c))
Acenaphthylene	>>140	3550	3.9	3.74(USEPA,1980(d))
1,4-dichlorobenzene	>662	6739	79	3.15(USEPA,1980(e))

- (1) Carbon capacity in mg/g.
- (2) Initial breakpoint in bed volumes treated.
- (3) Data from Dobbs and Cohen (1980).
- (4) K_{ow} = n-octanol/water partition coefficient. References given in parentheses.

The aqueous solubility-carbon sorption relationship has been most thoroughly investigated by Giusti et al. (1974). Working with 93 petroleum related organic compounds, they found that carbon capacity in batch reactors increased as aqueous solubility decreased for all compounds tested. Inspection of Table 45 reveals that this relationship was supported in the single-solute, continuous-flow systems employed in this study as well. Again, the only inconsistency observed in the experimental data is a reversal in the position of 2,4-dimethylphenol and dimethyl phthalate. The aqueous solubility-carbon capacity correlation is particularly evident among compounds from the same class of organic solutes, an observation also noted by Giusti et al. (1974).

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Several investigators have demonstrated that n-octanol/water partition coefficients (K_{ow}) and adsorption of hydrophobic organics on sediment materials are well correlated. Briggs (1973) developed a linear regression equation relating the soil sorption of phenyl urea herbicides to their n-octanol/water partitioning. Using a quantitative approach, Karickhoff et al. (1979) demonstrated that adsorption of several hydrophobic organics on sediment particulates produced linear isotherms which are similar to those obtained from activated carbon adsorption studies. From these data they developed a linear correlation between adsorbate K_{ow} values and the slope of the sediment adsorption isotherm, indicating that the extent of sediment adsorption could be predicted from K_{ow} values. According to these investigators findings, a larger K_{ow} value should indicate greater adsorbability. However, inspection of Table 45 reveals that for the compounds used in this study, no such simple correlation between K_{ow} values and carbon capacity could be found. K_{ow} values for these compounds would indicate significantly different carbon affinities than those observed in this study, even on a relative basis.

These data indicate that in simple matrices both aqueous solubility and batch adsorptive capacity provide useful tools for predicting relative carbon affinity in column applications. Although K_{ow} values were poorly correlated with carbon capacity for study compounds, the relationship merits further investigation. A possible explanation for the poor correlation observed for these compounds relates to their relatively high aqueous solubility. The soil adsorption - K_{ow} relationships were developed on very low solubility compounds (<2mg/l) and applicability may well be limited to this solubility range. Also, as noted by Karickhoff et al. (1979) literature K_{ow} values for a given compound are highly variable because of the use of poor analytical methodologies and/or the use of a variety of experimental protocols to make K_{ow} measurements. The data used for both solubility and K_{ow} comparisons were taken from EPA documents, which in turn were obtained from diverse literature sources. Because similar discrepancies exist in literature data for aqueous solubility measurements, it is possible that the inconsistencies observed between carbon system data and both of these parameters are related to the accuracy of the data selected.

Although batch adsorption data and adsorbate characteristics are useful for establishing relative adsorbate affinity, the lack of information concerning the shape of the breakthrough curve remains a limitation in application of these parameters to even simple continuous-flow matrices. The initial breakthrough point, defined as the point (expressed in cumulative volume treated) at which the compound is first detected in carbon column effluents, is an important characteristic of the breakthrough curve. This characteristic was selected as a representative parameter for comparative purposes. Solubility, K_{ow} , and batch data were inspected to determine if any of these parameters provided information regarding the point at which breakthrough initially occurred. Batch isotherm parameters considered included both capacity and isotherm slope. The slope of a batch isotherm is a measure of adsorption intensity, with smaller slope values indicative of greater adsorption intensity. The data in Tables 44 and 45 reveal that none of the four parameters considered provide an adequate indication of even the order of initial solute appearance. Particularly noteworthy is the poor correlation between any of the parameters and the initial breakthrough of acenaphthylene. Although

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acenaphthylene is one of the two highest capacity compounds tested, initial breakthrough occurred before all compounds except for phenol. From this limited data, any predictions of such breakthrough characteristics, of obvious significance in water or wastewater treatment applications, appears to be tenuous, at best.

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COMPETITIVE ADSORPTION STUDIES

High Spike Level Matrices

Multiple solute DIW and wastewater matrices were used to examine competitive adsorption phenomena. In the initial investigation, compounds previously run in single-solute systems were combined in a DIW matrix. Each compound was added at the concentration used in single solute studies, resulting in an equimolar (except acenaphthylene) six-component adsorption matrix. Two distinct advantages were realized with this design: 1) it enabled direct comparison of single and six-solute capacity data (since influent levels were comparable); and, 2) it assured that competitive adsorption phenomena would not be influenced by concentration effects.

Data obtained from this investigation indicate that competitive adsorption results in significant reduction in adsorptive efficiency for individual solutes. Examination of the single-solute capacity data (Table 33) reveals that carbon capacity for phenol and dimethyl phthalate was the lowest of the six compounds tested. Similarly, these data suggest that diethyl phthalate and 2,4-dimethylphenol are intermediate affinity components, with 1,4-dichlorobenzene and acenaphthylene exhibiting the highest affinities of the compounds tested. The composite plot of the adsorption of all compounds from the six-solute DIW matrix, presented as Figure 32, shows that with one exception, relative carbon affinities established in single-solute systems are unchanged in the competitive adsorption environment. As a result of the relatively weak carbon affinity for phenol and dimethyl phthalate, maximum adsorptive capacity for these solutes occurred considerably faster in the six-component matrix. In the multiple-solute system, the maximum adsorptive capacity for phenol occurred five times faster than in the single-solute run (Figure 4). In the mixed solute system maximum adsorptive capacity for dimethyl phthalate occurred in less than one-fourth the run time required in the single-solute adsorption matrix (Figure 5). The breakthrough patterns for these two relatively low affinity compounds of the six-solute matrix were quite similar (Figure 32).

Breakthrough curves for the two intermediate affinity components of the multiple solute DIW system, 2,4-dimethylphenol and diethyl phthalate, were also very similar (Figure 32). In the six-component matrix breakthrough of these compounds was greatly accelerated. The maximum carbon capacity for diethyl phthalate occurred about two times more rapidly than in the single-solute run (Figure 6). 2,4-dimethylphenol attained its maximum capacity six times faster in the multiple-solute matrix (Figure 7). The composite plot of the multiple-solute system shows that in this matrix carbon capacity for diethyl phthalate is substantially greater than for

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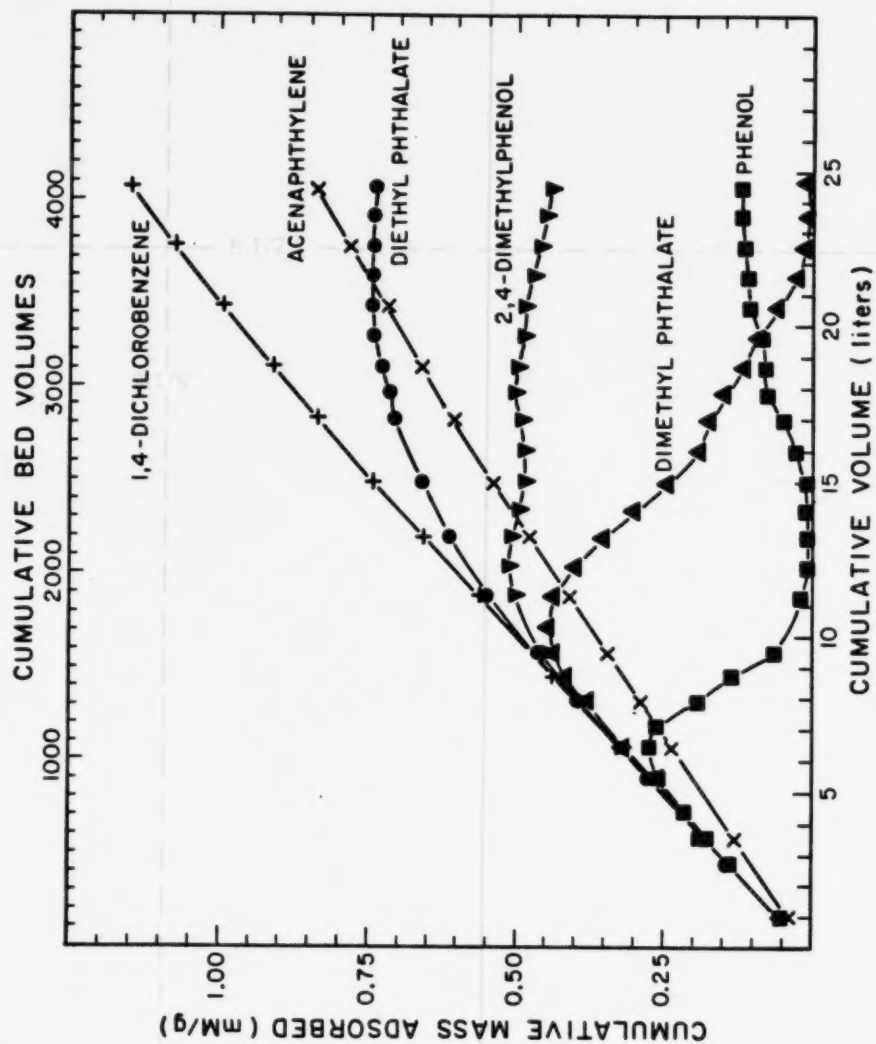


Figure 32. Effects of adsorption competition from a six-solute deionized water matrix.

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2,4-dimethylphenol. However in the single-solute runs, carbon capacity for 2,4-dimethylphenol was considerably greater than that for diethyl phthalate, indicating that 2,4-dimethylphenol should compete for adsorption sites more successfully in the mixed-solute system. This anomaly suggests that carbon affinity for certain organic species in multiple component matrices includes factors not expressed in single-solute capacity determinations. Molecular size, steric considerations, and ionization interactions may offer certain molecules a competitive advantage not obvious from inspection of simple, single-solute data. This inconsistency hints at the complexity of competitive adsorption phenomena occurring in even relatively simple water matrices.

Data on adsorption of acenaphthylene and 1,4-dichlorobenzene are presented to the point at which the effluent concentrations are approximately 10% of the respective influent levels (Figures 8 and 9). Maximum carbon capacity had not been reached for either solute within the column run times used in both single and six-component systems. Although from inspection of the shapes of the curves there appears to be little suppression of carbon capacity for these two compounds in the mixed solute matrix, the 10% breakthrough points did occur earlier. Of these two compounds, the 10% breakthrough data suggest that acenaphthylene is the highest affinity component. The 10% breakthrough point for 1,4-dichlorobenzene occurred almost four times more rapidly in the six-solute matrix than in the single solute run, but the 10% breakthrough points for acenaphthylene were almost identical. As evidenced by the composite plot of the mixed-solute matrix (Figure 32) 1,4-dichlorobenzene and acenaphthylene are clearly the most successful competitors for available adsorption sites. Competitive adsorption from these two higher affinity compounds was undoubtedly largely responsible for the accelerated breakthrough of the phenolic and phthalic acid species in the six-solute adsorption matrix.

Carbon capacity data offers further evidence that 1,4-dichlorobenzene and acenaphthylene are the highest affinity compounds of the solutes used in these investigations. In the six-solute DIW matrix, carbon capacity for individual phenolic and phthalic acid solutes was 61-80% less than that observed in the single-solute studies (Table 33). Of the four compounds which reached complete breakthrough within the duration of these two column runs, the two phenols exhibited the greatest reductions in adsorptive capacity in the mixed-solute system. Comparison of the combined adsorptive capacity for phenol, 2,4-dimethylphenol, dimethyl phthalate, and diethyl phthalate at selected points in the multiple component run with single solute adsorption capacities, indicates that the reduction in adsorptive capacity for these compounds is largely attributable to competitive adsorption from 1,4-dichlorobenzene and acenaphthylene. These data are summarized in Table 46 below.

The maximum combined adsorptive capacity for the four phenolic and phthalic acid solutes at any point in the six-solute run is approximately 1.48mM/g. The data in Table 46 show that this combined capacity value is less than the maximum adsorptive capacity of any common solute when run in a single-solute system, with the exception of phenol. It is also significant that the maximum combined capacity for these solutes occurred in the middle of the run, with subsequent column operation resulting in decreased combined capacity. Two observations provide undisputable proof

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TABLE 46. COMPARATIVE ADSORPTION FROM SINGLE- AND SIX-SOLUTE MATRICES

Pt of Interest ⁽¹⁾	Six-Solute DIW Run		Single-Solute DIW Run	
	Combined Capacity ⁽²⁾		Component	Max. Capacity ⁽³⁾
A	1.23		Phenol	1.19
B	1.47		2,4-dimethylphenol	2.63
C	1.48		Dimethyl Phthalate	1.62
D	1.41		Diethyl Phthalate	1.94
E	1.30			

- (1) Points of interest are as follows:
- A) point at which phenol reached maximum adsorption capacity;
 - B) point at which dimethyl phthalate reached maximum adsorptive capacity;
 - C) point at which 2,4-dimethylphenol reached maximum adsorptive capacity;
 - D) point at which diethyl phthalate reached maximum adsorptive capacity; and,
 - E) termination of the column run.
- (2) Combined adsorptive capacity of phenol, 2,4-dimethylphenol, dimethyl phthalate, and diethyl phthalate in mM/g.
- (3) Maximum adsorptive capacity in mM/g.

that competitive adsorption from 1,4-dichlorobenzene and acenaphthylene molecules was responsible for the greatly reduced carbon affinity for the other four species: 1) despite the fact that the six-fold higher combined influent concentration should result in greater carbon capacity in the multiple-solute system, the maximum combined capacity for the phenolic and phthalic acid solutes was less than the single-solute capacity for three of the four compounds; and, 2) the combined adsorptive capacity for the phenols and phthalates was decreasing late in the column run while 1,4-dichlorobenzene and acenaphthylene were still being removed at greater than 90% efficiency.

When these same six compounds were spiked into the industrial wastewater matrix at comparable concentration levels, very similar adsorption patterns were observed for all of the compounds (Figure 10). Similarly, comparison of carbon capacity values obtained from DIW and wastewater matrices shows only slight decreases for adsorption from the wastewater matrix (Table 34). These data indicate that the six spiked compounds were still the dominating force in the wastewater matrix, and that competitive adsorption from other wastewater constituents was minimal to the point at which the run was terminated. The only obvious effect of the presence of background components was the earlier initial breakthrough of all spiked compounds in the wastewater matrix (Table 34). Initial solute breakthrough occurred from 1.6 to 4.2 times faster in the wastewater matrix.

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The relatively small influence of background wastewater components is quite likely a function of relative concentration levels. In the wastewater matrix, spike components were present at roughly 500-1000 times greater concentration than background constituents, thus affording them a significant advantage in competition for available adsorption sites. This phenomenon has been observed by other investigators in simpler adsorption systems. Working with substituted phenols in DIW batch adsorption systems, Murin and Snoeyink (1979) observed that altering the relative concentration levels of two competing species could even result in changes in system domination. The effect of concentration on competitive adsorption phenomena also provides a possible explanation for the earlier breakthrough of spiked compounds, but comparable ultimate capacity observed in the wastewater system. Initially background wastewater components were moderately successful in competing for adsorption sites, resulting in less than optimal adsorption conditions for spiked components and some low-level leakage. However during subsequent column operation the large concentration difference may have afforded spike components so great a competitive advantage that they were able to replace previously adsorbed background components. Thus, although low level leakage of spiked components occurred throughout the column run, replacement of previously adsorbed species would allow comparable ultimate capacities to be attained. The early initial leakage observed in the competitive adsorption environment has important implications in treatment applications, particularly where a relatively low effluent toxicant level is required. Although overall removal capacity may be quite good, competitive adsorption may result in unacceptable effluent levels so early in the carbon bed life that economic feasibility of such treatment would be threatened.

The competitive adsorption patterns observed in the six component adsorption matrices are generally consistent with results obtained by other investigators. The data clearly demonstrate that competitive adsorption from the two higher affinity compounds resulted in considerable capacity reduction for lower affinity ones (60-81%) but the presence of lower affinity species had minimal effect on adsorption of the high affinity constituents. Similar observations were noted by Weber and Morris (1964) for competitive interactions between phenol and dodecyl benzene sulfate (DBS) molecules. Working with batch adsorption systems, they found that the presence of DBS resulted in a substantial reduction in carbon capacity for phenol, but the effect of phenol on DBS removal was minimal. They concluded that this phenomenon was the result of relative molecular size, the DBS molecule being considerably larger than the phenol molecule. The rationale advanced by these authors was that a DBS molecule, once having entered a pore of nearly molecular size, blocked access of that pore to subsequent entry of phenol molecules. Thus, pore constriction resulted in decreased capacity for phenol molecules. In the current investigation, this theory inadequately accounts for the enhanced carbon capacity observed for acenaphthylene and 1,4-dichlorobenzene. The phthalate esters and acenaphthylene are of comparable molecular size, and all three are larger than the 1,4-dichlorobenzene, yet carbon capacity for the phthalate esters was substantially lower than either in the mixed solute system. However, the difference in molecular size of the molecules used in this study may have been of insufficient magnitude to cause the competitive adsorption effects observed by Weber and Morris (1964). Thus

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molecular size can not be dismissed as a factor in competitive adsorption, but phenomena observed in these and subsequent studies indicate that other factors are also quite influential. The issue of carbon affinity will be addressed more thoroughly in subsequent discussions of these and other adsorption systems.

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Low Spike Level Matrices

Eleven- and twelve-solute DIW and wastewater adsorption matrices were used to further investigate the effects of matrix complexity on adsorptive phenomena observed in previous single- and six-solute systems. The DIW matrices served as a baseline for assessing the effects of increased matrix complexity in the comparable wastewater runs. In the well defined DIW matrix, adsorptive interactions were attributable only to competitive adsorption from other spiked compounds. Thus, capacity reductions and breakthrough characteristics observed in identically spiked wastewater matrices could be compared with those observed in the DIW systems to evaluate the extent of competitive adsorption from other background wastewater constituents.

To circumvent the problem of system domination by spiked components in the wastewater matrix, spike levels were lowered to $5\mu\text{M}$ in both eleven- and twelve-solute studies. Inspection of the data in Tables 35-38 reveals that at the lower spike concentration background wastewater constituents were quite effective in competing for available adsorption sites in both eleven- and twelve-solute matrices. A comparison of toxicant breakthrough levels from the twelve-component DIW and wastewater matrices is presently graphically in Figure 33. The 28.8 liter mark represents the point at which the wastewater column run was terminated, and is thus used for comparison. It is apparent at this point in the column runs that competitive adsorption from background wastewater components has resulted in substantial reductions in removal efficiency for all of the spiked compounds. A more thorough discussion of the adsorptive behavior of spiked components observed in these systems is presented in the following two sections.

Selective Adsorption Phenomena

Selective adsorption phenomena observed in the low spike level DIW and wastewater matrices generally closely followed those exhibited in the higher spike level, six-solute system. The presence of additional spike compounds and background wastewater constituents exerted little influence on the adsorption patterns of components common to low and high spike level matrices. Carbon affinities established in eleven- and twelve-solute systems, and in both DIW and wastewater matrices, were consistent with six-solute studies, decreasing according to the following general trend: PNA's = semivolatiles chlorinated hydrocarbons (hexachloroethane and 1,4-dichlorobenzene) > disubstituted phenols > phthalate esters >

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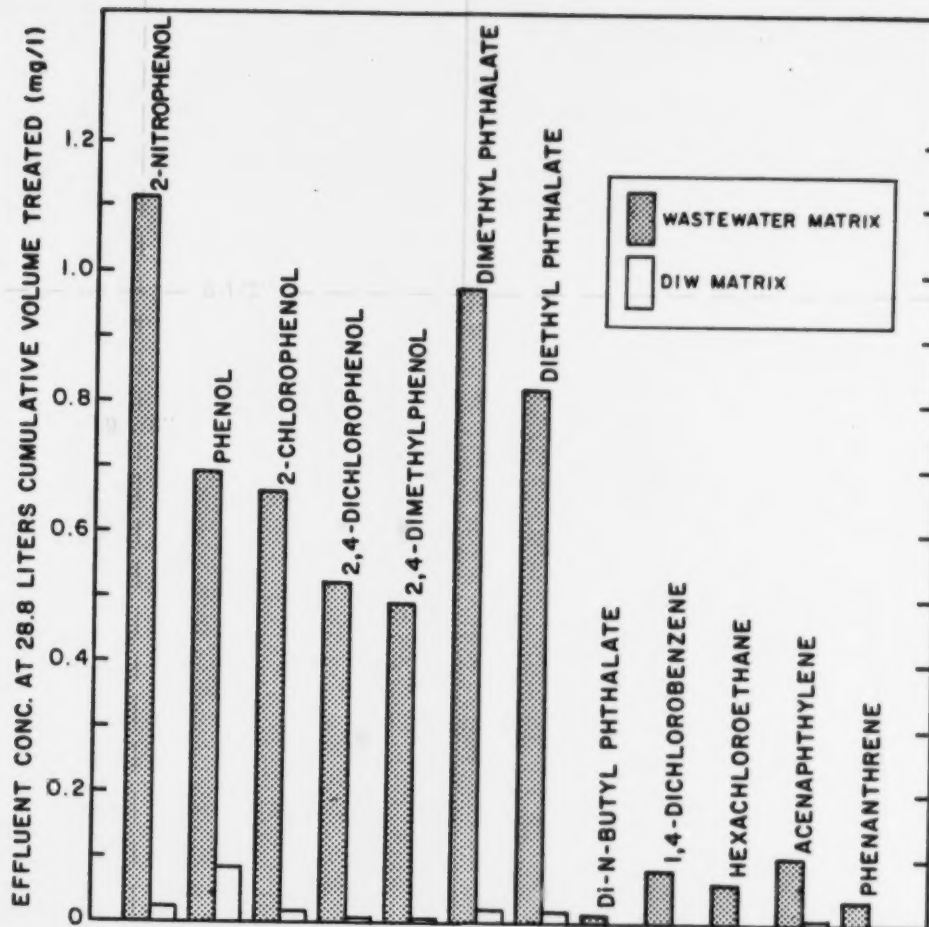


Figure 33. Effluent toxicant levels from twelve-component matrices.

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1,1,2,2-tetrachloroethane $\approx$ monosubstituted phenols > phenol. There were however several notable exceptions to this pattern, including: 1) low affinity for 2-nitrophenol in the wastewater matrices; 2) apparently greater affinity for the phthalates in the eleven-solute wastewater matrix; and, 3) apparently greater affinity for phenol in the eleven-solute wastewater matrix.

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The lower carbon capacity for 2-nitrophenol in both wastewater matrices (as compared with the corresponding DIW matrices) was undoubtedly a function of solution pH. The spiked DIW matrices had a pH of roughly 6.0, whereas the pH of both spiked wastewater systems was about 8.2. At pH=8.2 approximately 90% of the 2-nitrophenol present is in the anionic form ($pK_a=7.17$). In the ionic form 2-nitrophenol is considerably more water soluble, and is thus less adsorbable. The suppressed capacity for 2-nitrophenol at high pH is consistent with results obtained by Ward and Getzin (1970) for aromatic acids, and also with those observed by Murin and Snoeyink (1979) for chlorinated phenols. Wastewater pH exerted minimal influence on adsorption of the other phenolic compounds because of their relatively high pK_a values. 2-chlorophenol was the only other spiked compound with a pK_a value low enough to be influenced by the higher wastewater pH. However, the wastewater pH was slightly less than the pK_a for 2-chlorophenol ($pK_a=8.5$) and was therefore considered to exert only a minimal effect on adsorption of this compound. Although approximately 50% of the 2-chlorophenol is dissociated at the wastewater pH, results of studies on the adsorption of aromatic acids by Ward and Getzin (1970) suggest that adsorption of dissociable species reaches a maximum near $pH=pK_a$.

Extensive biological growth observed in the carbon columns treating the eleven-component wastewater matrix suggests that the apparently enhanced carbon capacity for phenol and the phthalate esters was a result of biodegradation within the column. A series of experiments were performed to determine whether biological activity was resulting in column influent alteration within the column reservoir. Triplicate samples of fresh column influent of known chemical integrity were "inoculated" with 10 ml of 20-hour old column reservoir solution. These samples were then incubated at room temperature for 24 hours (the maximum reservoir retention time) extracted, and analyzed to determine sample composition. The concentration values for spiked components obtained from these analyses were compared with similar values determined at the initiation of the study. The t-test statistic was employed for these comparisons, and no statistical difference between mean concentration values was observed for any spiked compound at the 95% significance level. These data were interpreted to mean that any biodegradation which occurred took place in the carbon column itself; not within the column reservoir. Although no experiments were undertaken to investigate the reasons for the apparent biodegradation in the eleven-component system but absence of such a phenomenon in the comparable twelve-component run, differences in composition of the indigenous biological communities provides one possible explanation. Wastewater samples used for the twelve-solute study were collected in late summer (8-79) whereas those used in the eleven-solute runs were collected in early spring (5-80). Samples collected on the 5-80 trip may well have contained bacterial species

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capable of utilizing phenol and phthalate substrates which were either not present, or viable, in the wastewaters collected on the late summer trip. This finding has an important implication in wastewater treatment applications. These data suggest that seasonal variation may affect changes in the biological composition of secondarily treated wastewaters, resulting in significant changes in GAC removal efficiency for some toxicants. Phenomenon such as this would complicate prediction of GAC performance, and make effective column monitoring even more difficult.

Neglecting solution effects, such as pH, and phenomenon such as biologically enhanced removal, toxicant removal efficiency in GAC adsorbers is a function of the intensity of adsorbate-adsorbent affinities. In competitive adsorption environments such as those encountered in wastewater treatment applications, a strong adsorbate-adsorbent affinity results in more effective competition for GAC adsorption sites. The enhanced removal of high GAC affinity compounds in competitive adsorption environments results not only from more successful adsorption on mutually available adsorption sites, but also from adsorption on sites not available to other solutes. Although somewhat apparent in eleven- and twelve-solute studies, the phenomenon of site specificity is particularly apparent in the six-solute DIW matrix. The composite plot of this system (Figure 32) shows that the substantially greater carbon capacity for 1,4-dichlorobenzene and acenaphthylene is at least partially attributable to site specific adsorption. From a comparison of summations of the mM/g of all compounds adsorbed at the 6.5, 10, and 21-liter run volumes, it becomes apparent that at the 6.5- and 10-liter volumes there are many remaining adsorption sites that are not accessible to phenol or dimethyl phthalate molecules. Maximum carbon capacity for phenol and dimethyl phthalate occurred at the 6.5- and 10-liter volumes, respectively, but at 21 liters treated, carbon adsorption for both was near zero. However, the combined molar capacity at the 21-liter volume was greater than that at either previous point, indicating that the continued removal of 1,4-dichlorobenzene and acenaphthylene resulted not only from replacement of previously sorbed species, but also from adsorption at sites unavailable to other solutes. These data support the theories advanced by Weber and Morris (1964) and Jain and Snoeyink (1973) that some portion of the surface of active carbons contain sites so specific for certain species that competitive adsorption from other compounds is virtually excluded. Chemisorptive bonding between carbon surface functional groups and appropriate adsorbate molecules provides the best explanation for this selective adsorption phenomenon.

Breakthrough Characteristics of Treatment Application Significance

Several adsorptive phenomena observed in both high spike level, six solute matrices and low spike level, eleven- and twelve-solute matrices are of particular importance in application of GAC adsorption to water and wastewater treatment systems. These adsorptive phenomena or characteristics also provide useful criteria for evaluation of GAC affinity for the organic toxicants used in these studies.

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Carbon affinity for organic toxicants is the key focal point, because it is a primary factor determining treatment feasibility. The use in this study of a relatively diverse group of organic toxicants in both well defined DIW and very complex wastewater matrices allows a more thorough examination of both the scope of adsorbate-adsorbent affinities and the consistency of these affinities in a range of competitive adsorption environments. Adsorptive characteristics considered particularly important in examining GAC treatment efficiency include: toxicant elution order or initial toxicant breakthrough; the shape of the breakthrough curve for individual toxicants; and, desorption phenomena.

Initial Breakthrough/Elution Order

For toxicants which can be initially removed to below the detection limit with fresh GAC, such as the compounds used in these studies, the point of initial breakthrough (or detection) is of treatment significance. This point provides the first indication that available adsorption sites for the given compound are becoming limited, and carbon capacity for this compound is approaching exhaustion. Initial toxicant breakthrough is also particularly important because of its relation to column monitoring. Once a toxicant of interest or monitoring significance has been detected in the carbon column effluent, subsequent column operation requires even more careful monitoring to insure that effluent concentration levels remain within acceptable limits (by whatever criterion is applied).

Comparisons of initial breakthrough points between single- and six-solute DIW matrices, and multiple solute DIW and wastewater matrices, reveal that competitive adsorption not only results in carbon capacity reductions, but also in accelerated initial toxicant breakthrough. In the six solute DIW matrix initial breakthrough occurred from 7.5 to 24.8 times more rapidly than in the single solute runs (Table 33). Initial breakthrough in the six solute wastewater matrix occurred only slightly faster than in the comparable DIW matrix because of system domination by spiked compounds (Table 31). In eleven- and twelve-solute wastewater matrices, initial toxicant breakthrough occurred from 2.3 to 12.8 times more rapidly than in the corresponding DIW matrices (Tables 35-38). A distinct pattern emerged in the low spike level matrices in which competitive adsorption from wastewater constituents resulted in: 1) phenolic species exhibiting the most pronounced acceleration of initial breakthrough (6.3 to 8.3 X faster); 2) phthalates exhibiting intermediate acceleration (all 4.3 X faster); and, 3) the highest carbon affinity compounds, chlorinated hydrocarbons and PNA's, exhibiting the least acceleration of breakthrough (2.3 to 3.1 X more rapidly). The correlation between accelerated initial breakthrough in the wastewater matrix and carbon affinity (as indicated by capacity or percent breakthrough at run termination) was quite good in all cases except for the disubstituted phenols. These compounds were shown to be high affinity components, yet competitive adsorption in the wastewater matrix resulted in the greatest acceleration in initial breakthrough of

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The order of initial toxicant appearance, or elution order, (summarized in Table 47 below) proved to be fairly consistent in all experimental matrices. The apparent inconsistencies in the elution order of several compounds is likely a function of the manner in which column effluent samples were collected. Inspection of Table 47 reveals that in a number of instances several toxicants were initially detected at the same point in the column run. Because effluent samples were collected at roughly one-liter intervals, it was not possible to determine the exact point of breakthrough for a given compound. Thus when several spiked compounds were initially detected in a given effluent fraction, it was impossible to tell the order in which initial breakthrough of those compounds actually occurred. With the dramatic exception of the phthalates, and to a lesser extent acenaphthylene, elution order or initial breakthrough followed the pattern which would be predicted from carbon affinity/capacity considerations. Although contamination is always a particularly prominent possibility with phthalates, it was not considered to be a factor in the early initial breakthrough observed for these compounds because phthalates were not detected in the first few effluent fractions collected. The relatively rapid initial breakthrough of these high carbon affinity compounds is closely related to the shape of their respective breakthrough curves.

TABLE 47. TOXICANT ELUTION ORDER IN EXPERIMENTAL ADSORPTION MATRICES

Compound	Toxicant Elution Order ⁽¹⁾					
	Six-Solute		Twelve-Solute		Eleven-Solute	
	DIW	WW	DIW	WW	DIW	WW
1,1,2,2-tetrachloroethane	-	-	-	-	1	1
Dimethyl Phthalate	1	1	1	1	3	3
Diethyl Phthalate	2	1	1	1	3	2
Di-n-butyl Phthalate	-	-	1	1	2	2
Phenol	2	1	2	1	4	3
2-nitrophenol	-	-	3	1	5	2
2-chlorophenol	-	-	4	2	6	4
2,4-dimethylphenol	2	2	7	2	9	4
2,4-dichlorophenol	-	-	7	2	9	5
Acenaphthylene	2	1	6	3	8	7
Hexachloroethane	-	-	5	3	-	-
1,4-dichlorobenzene	3	2	5	4	7	6
Phenanthrene	-	-	7	5	-	-

(1) Compounds with the same number were initially detected in the same column effluent fraction.

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Perhaps of even greater significance in effective treatment applications is the rate of breakthrough, or the rate at which the effluent toxicant concentration increases after initial appearance. The breakthrough rate, or shape of toxicant breakthrough curves, has important implications on technological, economic, and monitoring aspects of GAC treatment. Rapid breakthrough is exemplified by compounds which progress from initial breakthrough to complete breakthrough within a relatively short period of column operation. Conversely, slow breakthrough is characterized by a prolonged period of low-level toxicant leakage, followed by a slow approach to complete breakthrough. Both slow and rapid breakthrough curves can be of great importance in successful use of GAC as a technique for control of organic toxicants.

Low carbon affinity toxicants exhibiting rapid breakthrough patterns determine both technological and economic feasibility of GAC treatment. Provided that rapid breakthrough of such compounds does not preclude GAC as a feasible treatment technology, they must become the focal point of column monitoring efforts to insure effective use of GAC technology. These compounds will not only likely require fairly specific monitoring techniques, but will also require more frequent monitoring to detect the point of carbon exhaustion for these compounds. Compounds displaying slow breakthrough curves may also be of monitoring concern, because initial breakthrough of these compounds generally occurred relatively early in the column run. Although maximum carbon capacity for compounds exhibiting this type of adsorption pattern was generally quite high, early initial breakthrough and subsequent low-level leakage occurred much earlier than expected from affinity considerations. In these investigations for example, initial breakthrough for several compounds displaying such adsorption characteristics occurred in advance of other very low affinity spiked toxicants.

Adsorption curves for selected toxicants from eleven component wastewater and DIW matrices representative of rapid, intermediate, and slow breakthrough patterns are presented in Figures 34 and 35, respectively. Results of these studies indicate that low carbon affinity compounds exhibited rapid breakthrough curves, but high affinity components displayed both types of breakthrough patterns. Figure 34 shows that in the wastewater matrix 2-nitrophenol, the lowest affinity spiked compound, progressed from initial to complete breakthrough in less than 3500 bed volumes. Conversely, with the elution of about 4700 bed volumes, breakthrough of acenaphthylene, a high affinity compound, was less than 10% complete. This phenomenon is even more pronounced for the phthalates, as indicated by the adsorption pattern for diethyl phthalate from the eleven solute DIW matrix (Figure 35). In this system, complete breakthrough of phenol occurred with 6500 bed volumes. Yet diethyl phthalate attained less than 10% breakthrough in 9000 bed volumes, even though initial breakthrough occurred 2500 bed volumes in advance of phenol.

Within the matrices employed in these investigations, phenolic species exhibited rapid breakthrough curves. This pattern was observed

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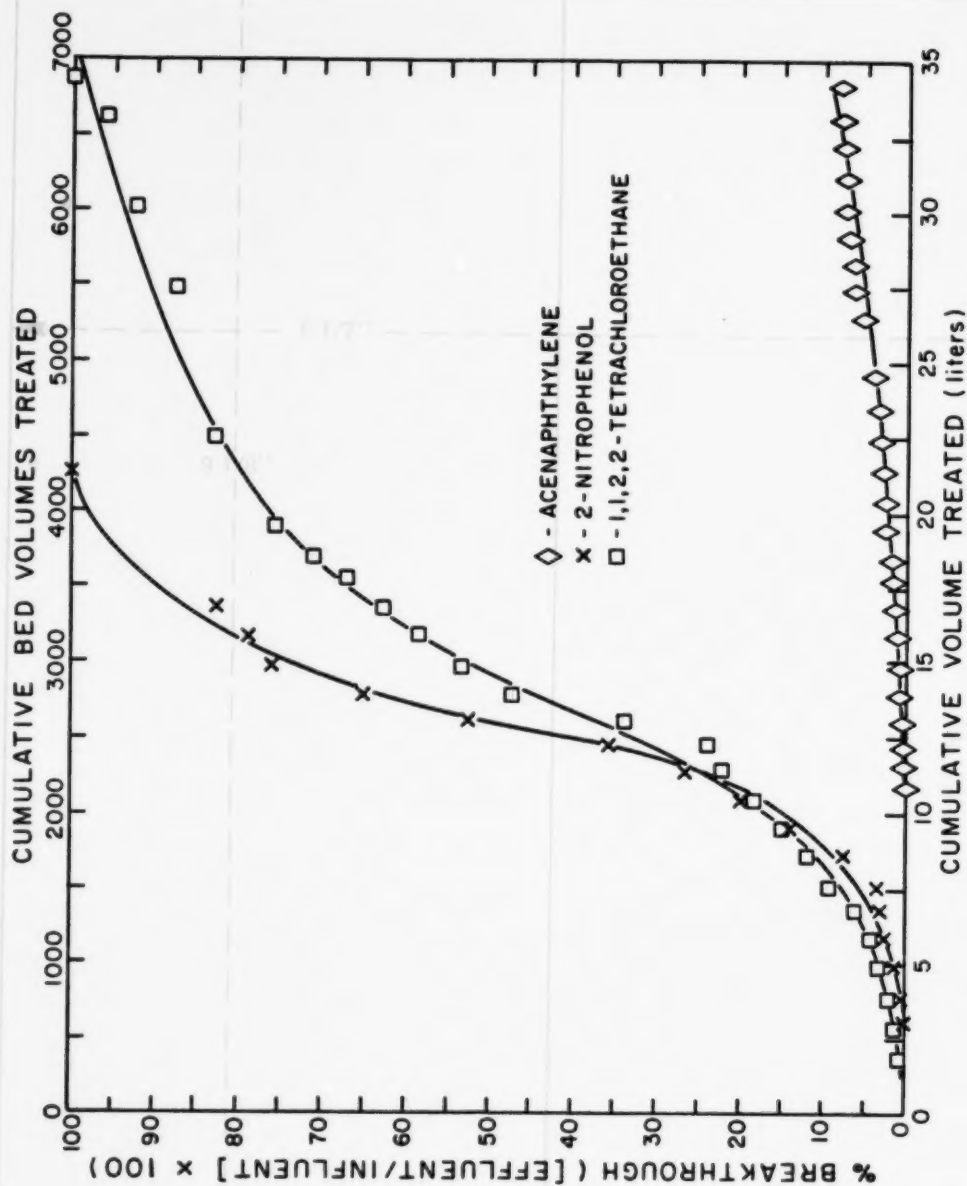


Figure 34. Toxicant breakthrough curves from eleven-component wastewater matrix.

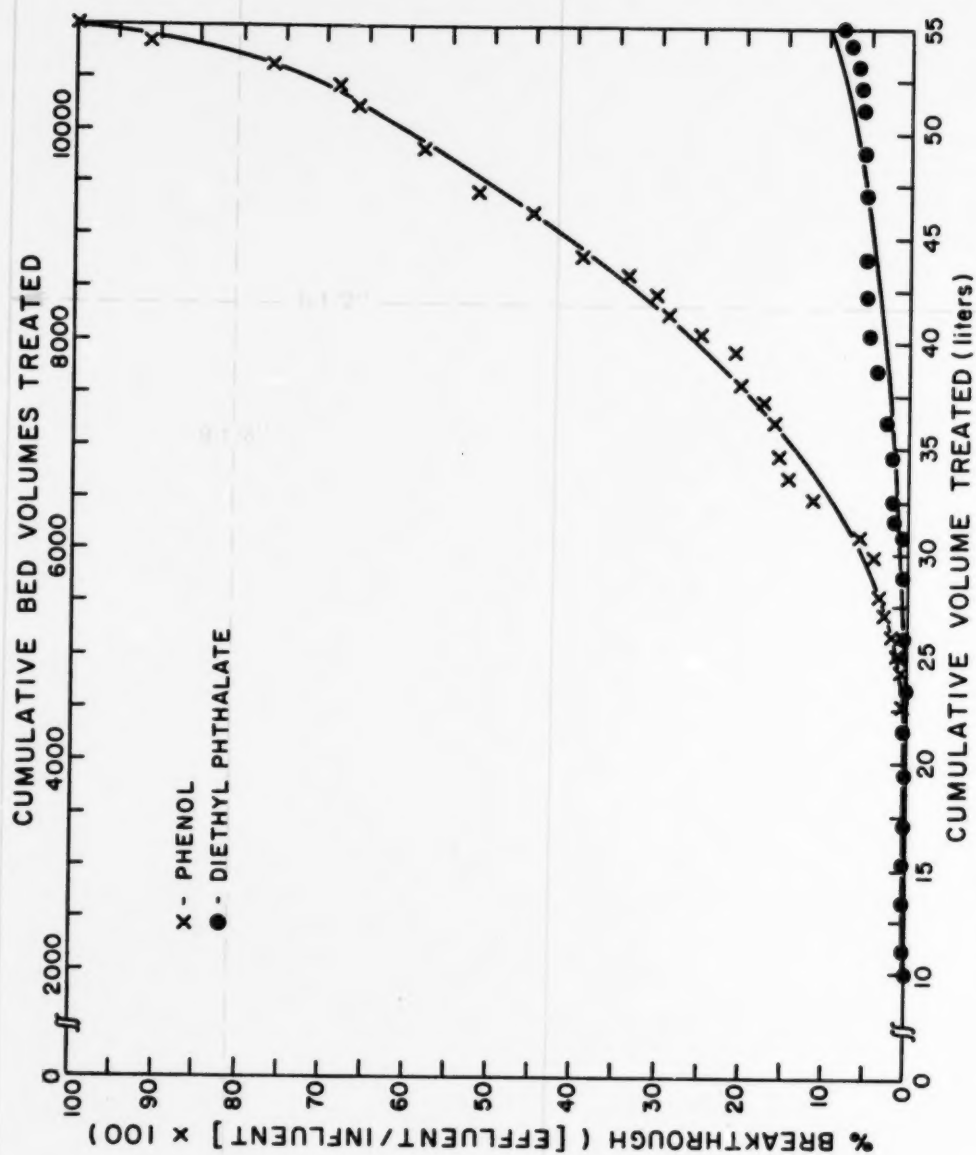


Figure 35. Toxicant breakthrough curves from eleven-component DIW Matrix.

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for both low affinity compounds (phenol and monosubstituted phenols) and relatively high affinity ones (disubstituted phenols). The phthalates, 1,4-dichlorobenzene, and acenaphthylene all exhibited slow breakthrough curves, while 1,1,2,2-tetrachloroethane proved to be an intermediate (Figure 34). The various breakthrough patterns observed in these studies are apparently a function of variations in the height of the mass transfer zone for the individual toxicants used, and the rate of movement of the mass transfer zone. The height of the mass transfer zone, or depth of the adsorption zone, is a measure of the rate of adsorbate removal in the mass transfer zone, while the rate of movement of the mass transfer zone is dependent upon adsorbent affinity for adsorbate molecules (Zogorski and Faust, 1976). Steep breakthrough curves are associated with shallow, relatively rapidly moving mass transfer zones, while flat curves are indicative of deep adsorption zones (Argaman and Eckenfelder, 1976).

Mass transfer zone characteristics provide an explanation for the unusual adsorption patterns observed for the phthalate esters (rapid initial breakthrough followed by a prolonged period of low-level leakage; hence large ultimate carbon capacity). The height of the mass transfer zone for these compounds is apparently deep, thus requiring a long section of the carbon column to affect 100% removal. If the height of the mass transfer zone for these compounds is of near column proportions, then a little movement of this zone would result in the leading edge progressing past the effluent end of the carbon column. Progression of the leading edge of the mass transfer zone beyond the end of the carbon column results in initial solute breakthrough, which would continue for the duration of column operation. However, provided that the majority of the adsorption of such compounds was occurring at the upper reaches of the long transfer zone, and that movement of this zone was slow, ultimate carbon capacity would still be quite high even though initial breakthrough was rapid. Slow movement of the mass transfer zone is characteristic of high affinity compounds, and in this context would account for the prolonged period of low-level leakage observed in these investigations.

Zogorski and Faust (1976) found that the height of the mass transfer zone was little influenced by adsorbate type, but that the rate of movement of the mass transfer zone was highly dependent upon adsorbate type. Data from the current investigations support the latter conclusion, but suggest that the height of the mass transfer zone is also adsorbate dependent. The more diverse group of adsorbates used in the current study, relative to those studied by Zogorski and Faust (1976) provides a likely reason for the discrepancy. These authors examined mass transfer phenomena using phenol and chlorinated phenols. These compounds were found to exhibit similar adsorption patterns in the current investigations as well, thus results were generally consistent with the observations of Zogorski and Faust (1976) when limited to common adsorbate species.

In the complex matrices used for these investigations, the interactions of carbon affinity and relative concentration level in the competitive adsorption environment may account for the relatively long mass transfer zone believed responsible for early phthalate breakthrough. Viewed in a column chromatography context, adsorption and desorption of solute molecules from carbon surfaces are occurring continually, with the exchange rate being a function of adsorbent affinity and relative concen-

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tration. Early in the column run, the majority of the high affinity components, and a portion of the lower affinity components, are adsorbed at the top of the column. Conversely, in the second increment of carbon column, most of the lower affinity components are adsorbed in the lesser competitive environment, along with a portion of the higher affinity compounds. However, it is conceivable that the small portion of higher affinity components are less successful competitors in the second increment of the column because of their now much lower relative concentration level. As a result the secondary adsorption band for these higher affinity compounds may actually be beneath the lower affinity components. Upon continued column operation, higher affinity components again not only out compete lower affinity components in the upper portion of the column, but now may also replace previously adsorbed lower affinity compounds. Thus the concentration advantage afforded lower affinity components in successive increments of the carbon column is even greater. Now the small portion of higher affinity species not removed in the upper section of column encounter even more rigorous competitive adsorption conditions in the successive column segments. The concentration gradient in lower column segments may even attain sufficient magnitude to allow replacement of higher affinity species by lower affinity ones. Repetition of these competitive adsorption phenomena could explain the apparently long mass transfer zone and subsequent rapid initial breakthrough of these high affinity compounds.

Conversely, lower affinity compounds exhibit rapid breakthrough patterns because the mass transfer zone for these compounds is kept compact and moves rapidly down the carbon column. Competitive adsorption confines removal of lower affinity compounds to the lower sections of the column, where in a competitively favorable environment, they are removed in a relatively short section of carbon. However, as carbon capacity for higher affinity compounds nears exhaustion in the upper reaches of the column, the mass transfer zone for these compounds moves down the column. At this point the mass transfer zone for lower affinity compounds is forced further down the column, with replacement of previously sorbed lower affinity components resulting in even more rapid mass transfer zone movement. Progressive movement of the mass transfer zone for higher affinity compounds thus results in quick movement of the shallow mass transfer zone characteristic of lower affinity compounds exhibiting rapid breakthrough curves.

In addition to contamination (discussed previously) as a possible explanation for the rapid initial breakthrough and subsequent low-level leakage observed for the phthalate esters, channeling must also be considered. Channeling, laminar solution flow along the column walls minimizing carbon contact time, is always a potential problem when small scale carbon columns are employed. However, although channeling undoubtedly occurred to some extent in these systems, the data indicate that this phenomenon was not a significant factor in defining adsorption curves. If channeling were a significant problem in the adsorption systems employed in these investigations, the effect should have been most pronounced on low carbon affinity components. Since the detrimental effect of channeling results from reduced carbon contact time, this phenomenon should result in most rapid initial breakthrough for low affinity components; with subsequent breakthrough of other adsorbates

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in the order of increasing carbon affinity. However, in both eleven- and twelve-solute DIW matrices, initial breakthrough of the phthalate esters (high carbon affinity compounds) occurred far in advance of initial breakthrough for phenol (a low affinity compound). Thus, provided that contamination was not a factor, the phthalate ester species would have to be selectively channeled for this phenomenon to account for the breakthrough patterns observed.

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Two other observations support the conclusion that channeling did not significantly influence results of lab-scale studies. Results from initial studies designed to optimize lab-scale column performance indicated that adsorptive capacity of the larger mesh carbon was comparable to smaller size fractions (Table 23). Also, phenol was initially detected at approximately the same point in the column runs, indicating that particle size exerted little influence on initial breakthrough. Capacity and initial breakthrough were found to be little influenced by carbon particle size in columns 2.5 times larger in diameter than those used in subsequent studies, as well as for those of equal dimensions (Table 23). Additionally, results from pilot-scale studies on adsorption of unspiked wastewater from the same facility show adsorption patterns similar to those observed in lab-scale systems. These data provide further evidence that channeling was not of sufficient magnitude to be a key factor in defining the shapes of breakthrough curves observed in lab-scale studies.

Desorption

In terms of human health and environmental quality, desorption undoubtedly represents the most detrimental potential consequence of GAC treatment of drinking waters and wastewaters. Desorption of previously adsorbed molecules can result in column effluent concentrations in excess of influent levels, actually deteriorating the quality of the untreated water. The ramifications of desorption are of obvious significance in effective use of GAC treatment as a technique for control of toxic organic chemicals. The potential expression of this phenomenon makes careful monitoring of carbon column effluents an absolute necessity if GAC treatment is to affect any degree of success in improving the quality of our drinking waters and aquatic environments.

Desorption of one or more of the toxicants of interest was observed in every spiked wastewater matrix run. Desorption was limited to the lower affinity components of each matrix, and was particularly evident in the higher spike level six-solute systems. Desorption of phenol and dimethyl phthalate (the two lowest affinity compounds in the six-solute DIW matrix) was quite extensive, with carbon capacity for both compounds eventually approaching zero (Figure 32). Column effluent levels reached values as great as 2.9 times that of the influent phenol concentration, and 2.4 times that of the influent dimethyl phthalate level. The subsequent desorption of 2,4-dimethylphenol and diethyl phthalate, the intermediate affinity components in this system, indicate that desorption was the result of competitive adsorption from those solutes with the greatest

carbon affinity. The difference in relative carbon affinities was of sufficient magnitude to cause replacement of previously sorbed lower affinity species. The desorption patterns provide further evidence that 1,4-dichlorobenzene and acenaphthylene are the highest affinity components in this matrix.

Desorption was not strictly an artifact of high influent concentration, as it was observed in both low spike level systems as well. At the 5 μ M influent level used in the twelve-solute wastewater matrix, four of the twelve spiked components were exhibiting desorption patterns by the time the run was terminated (Table 36 and Figure 11). Competitive adsorption from the higher affinity PNA's and chlorinated hydrocarbons again appears to be causing replacement of the lower affinity compounds. Similar desorption patterns were observed in both eleven-solute adsorption matrices, indicating that desorption of low affinity compounds will likely occur in any complex matrix. The desorption phenomena observed in these investigations are in agreement with patterns obtained by Symons (1978) from GAC studies where volatile organic toxicants were monitored, and also with results reported by Baker (1964) for desorption of n-butanol by n-ethyl acetate.

The implications of the three adsorption characteristics discussed here (initial breakthrough, breakthrough curve shape and desorption) on effective use of GAC for control of toxic organics illustrate the importance of continuous-flow adsorption studies. A knowledge of these adsorption phenomena is vital to successful use of GAC, from both technical and economic aspects. The exclusive use of batch adsorption studies to assess treatment feasibility results in little, if any, information regarding the existence and/or magnitude of these adsorption characteristics.

TOC AND COD AS COLUMN MONITORING TOOLS

The breakthrough curves for TOC and COD from both eleven- and twelve-solute wastewater matrices (Figures 12-17) indicate that a substantial portion of the organic material present in the wastewater matrix was not amenable to activated carbon adsorption. In the twelve-solute matrix, breakthrough of approximately 10% of the TOC constituents and 30-45% of the materials contributing to COD measurements had occurred by the first effluent fraction collected (140 bed volumes treated). In the subsequent eleven-solute wastewater runs, samples for TOC and COD analyses were collected at 5 bed volumes treated. Again a considerable portion of the organic constituents expressed as TOC and COD were totally unadsorbable (Figures 15-17). In this system an immediate TOC breakthrough of 15% was observed, while 5% (UV-correlation) to 30% (digestion) of the COD materials were unadsorbable. Chromatograms (presented in the Appendix, Figure A1) of the carbon column influent and first fifteen effluent fractions collected from the eleven-solute wastewater matrix provide some insight into the overall breakthrough pattern for the organics amenable to GLC analysis. Inspection of the chromatogram for the first effluent fraction collected (Figure A1-1) reveals that the unadsorbable organic species were not amenable to GLC analysis under the conditions used for these analyses (see Analytical Methods).

Breakthrough of wastewater background constituents was first detected in effluent fraction #2 (Figure A1-3) and subsequent breakthrough occurred quite rapidly (Figures A1-3 to A1-16). Wastewater background components appearing at 14-21 minute GLC elution times were not only the strongest peaks observed in the column influent, but also were least adsorbable of the compounds amenable to GLC analysis. Identification of these compounds was of interest because of both their low carbon affinity, and contribution to the rapid TOC/COD breakthrough. Column effluent fraction #4 was selected for GC/MS identification of these compounds; the GC/MS data on this sample is presented in the Appendix. The total ion chromatogram of effluent fraction #4 is presented in Figure A2. As a result of slightly different analysis conditions, the wastewater background components of particular interest appear at 19-26 minute elution times in the GC/MS analysis (Figure A2).

As evidenced by the three-dimensional plots of scan number vs. mass (Figure A3) the peaks appearing at 23-26 minute elution times (scan numbers 380-430) are apparently very similar compounds. Although the ionization mode employed in this analysis (electron impact at 70eV) precludes exact identification of these compounds because of lacking molecular weight data, the MS data indicates that these compounds are C10-C20 highly substituted alcohols. The nature of the wastewater (petrochemical origin) and low carbon affinity for alcohols both support the MS data. Other early breakthrough compounds identified by the GC/MS analysis are listed in Table 48.

TABLE 48. OTHER COMPOUNDS IDENTIFIED IN EFFLUENT FRACTION 4 BY GC/MS

RT ⁽¹⁾	Compound
3.7	n-heptane (likely an extraction solvent impurity)
4.6	phenylmethylhydrazine
5.9	1,1,2,2-tetrachloroethane (a spiked compound)
7.6	1,2-dimethylbenzene
11.8	1,2-dichlorobenzene (internal standard)
19.4	substituted cyclohexanecarboxylic acid

(1) Retention time in minutes (Refer to Figure A2).

The shape of the breakthrough curves for TOC and COD parameters from both low spike level wastewater matrices (Figures 12-17) were quite different from those observed for individual toxicants. Individual toxicants generally showed little breakthrough early in the run, and then progressed either slowly, or rapidly, to complete breakthrough. Conversely, the surrogate organic parameters exhibited rapid initial breakthrough, followed by a sustained period of 20-30% removal. The adsorption pattern observed for TOC and COD parameters in these studies is consistent with results for TOC breakthrough from surface water sources obtained by Glaze et al. (1981) and from humic and fulvic acid solutions obtained by Lee

and Snoeyink (1980). In the twelve-solute matrix TOC showed the least amount of unadsorbable materials of the three surrogate organic parameters examined (TOC, COD-digestion, and COD-UV correlation). The breakthrough rates for these parameters were comparable early in the run (0-1000 bed volumes) and late in the run (greater than 3500 bed volumes) with TOC exhibiting the most rapid breakthrough rate between these points (1000-3500 bed volumes). In the eleven-solute wastewater matrix where samples were collected very early in the column run for surrogate parameter determinations, breakthrough of COD by both methods of measurement was more rapid than that for TOC.

The following generalizations can be drawn from inspection of the breakthrough curves for the surrogate organic parameters from both wastewater matrices: 1) between the two matrices breakthrough curves for all three parameters were very similar; 2) within each of the matrices COD curves were very similar by both methods of measurement; and, 3) all three parameters appeared to be asymptotically approaching approximately 80% breakthrough.

If removal of specific toxic organics to some predetermined effluent level is to be the objective of GAC treatment, carbon column monitoring techniques must be sensitive to detection of such compounds in column effluents. Results from these investigations indicate that the radically different shape of the breakthrough curves observed for the surrogate monitoring parameters, vs the individual toxicants used in this study, will make effective column monitoring difficult, at best. Examination of the data reveals that two major inadequacies inhibit effective use of TOC or COD parameters as carbon column monitoring tools in the wastewater matrices used for these investigations. Both deficiencies are a function of the shape of the breakthrough curves displayed by the surrogate parameters.

The first inadequacy relates to the manner in which TOC or COD parameters are generally applied as monitoring tools. In typical applications, carbon exhaustion is indicated by a given percentage breakthrough of the monitoring parameter. Although no such criterion exists in wastewater treatment applications, carbon regeneration at approximately 50% TOC breakthrough is one of the recommended criteria in drinking water treatment applications. This approach to carbon column monitoring in wastewater treatment applications was evaluated by examining column effluent toxicant levels at various TOC/COD breakthrough points. The relationships between percentage breakthrough for the surrogate parameters and the breakthrough of selected toxicants from the twelve-solute wastewater matrix are presented graphically in Figures 36-38. In these graphs, breakpoints corresponding to approximately 25, 50, and 75% breakthrough ($\pm 4\%$) are indicated for TOC (Figure 36) COD-UV correlation (Figure 37) and COD-digestion (Figure 38).

In the spiked wastewater matrices used for these investigations, the rapid initial breakthrough and subsequent prolonged slow breakthrough patterns exhibited by all three surrogate parameters resulted in poorly defined breakthrough points. Although best fit curves could be drawn through individual data points to develop smooth breakthrough curves for surrogate parameters, it is evident from inspection of Figures 12-17 that breakthrough of these parameters did not follow a smooth progression. As a result of fluctuations in effluent TOC and COD concentrations, it was

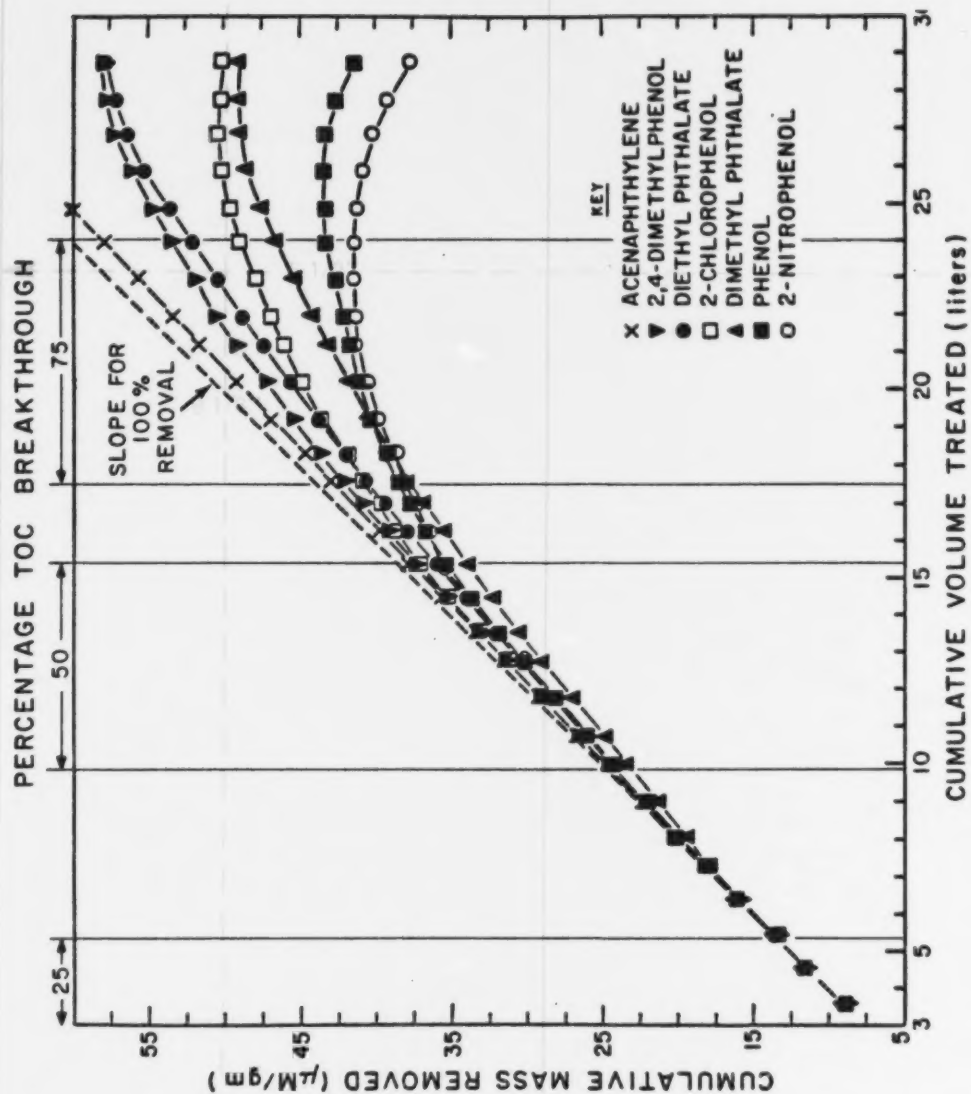


Figure 36. TOC breakthrough vs. breakthrough of selected toxicants from twelve-component wastewater matrix.

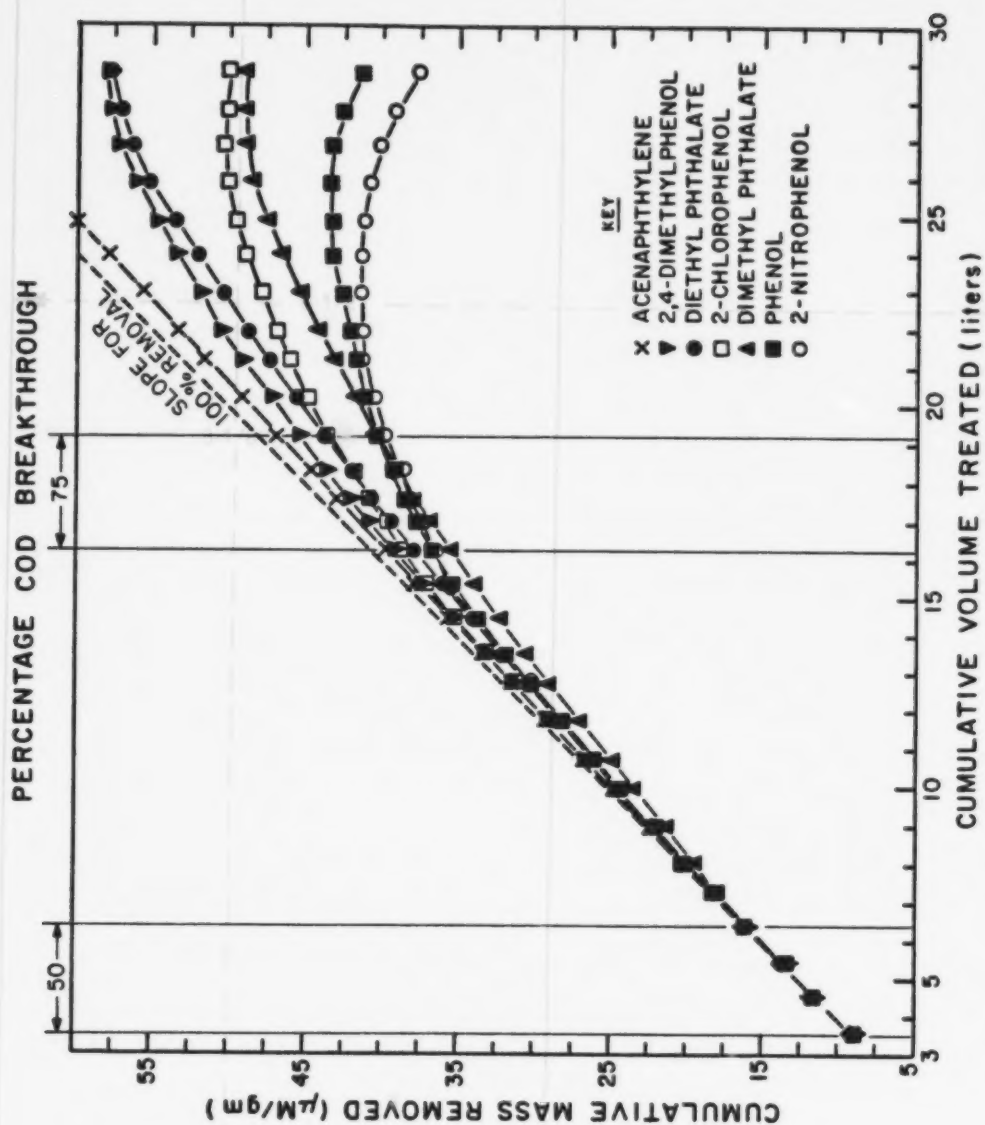


Figure 37. COD breakthrough (UV Correlation) vs. breakthrough of selected toxicants from twelve-component wastewater matrix.

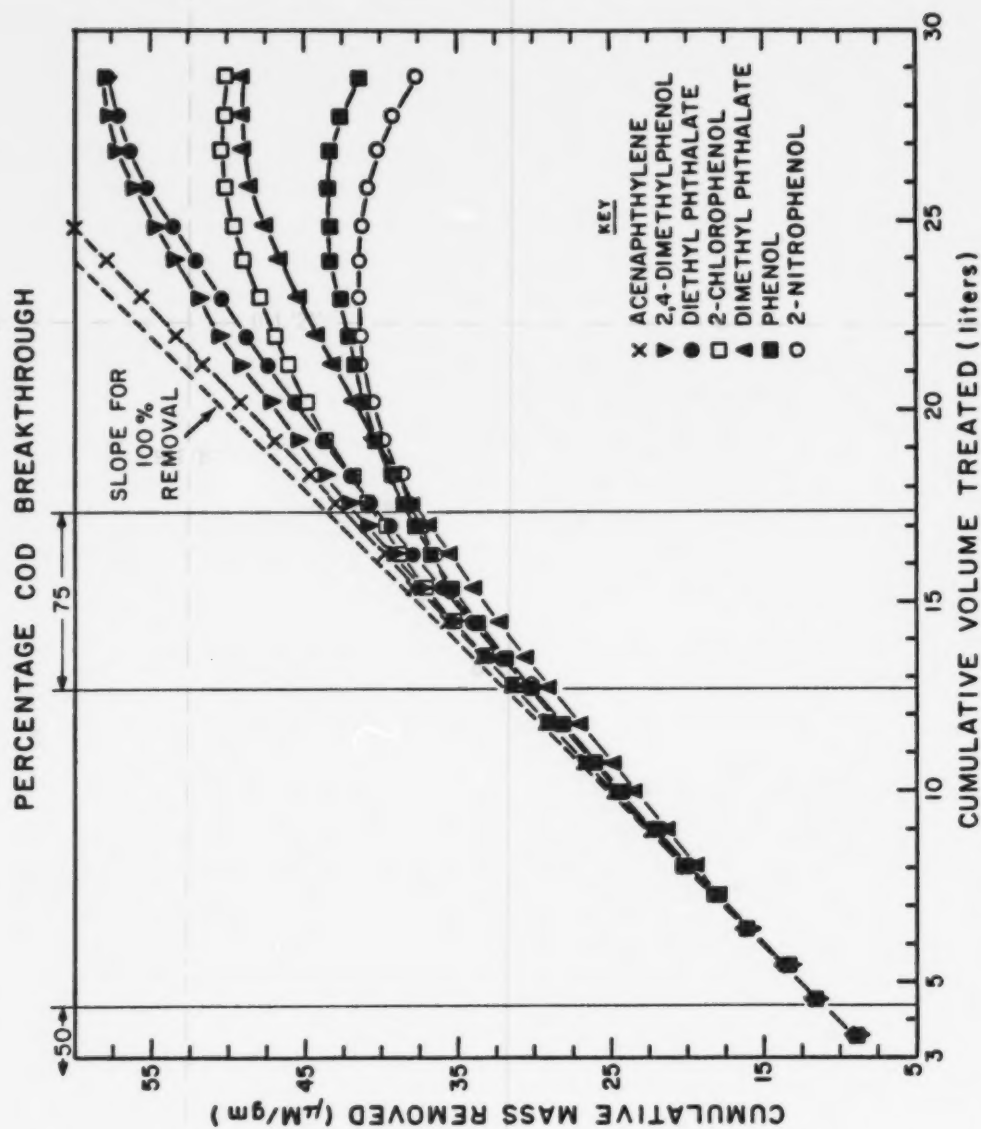


Figure 38. COD breakthrough (Digestion) vs. breakthrough of selected toxicants from twelve-component wastewater matrix.

very difficult to define a point within the column run at which a given percentage breakthrough occurred. Because of this phenomenon, breakpoint ranges or zones had to be used for surrogate parameters in evaluations of monitoring effectiveness.

Inspection of Figures 36-38 reveals that the percentage breakthrough approach to column monitoring was of dubious value for the adsorption systems employed in the current investigations. These data indicate that two types of problems exist when ambiguous breakthrough zones must be employed in place of discrete breakthrough points. Although the 25% TOC and 50% COD breakthrough zones occurred prior to significant toxicant leakage (thus providing adequate protection) ambiguity regarding when the point occurred could well result in regeneration far in advance of actual carbon exhaustion. Figures 36-38 show that significant increases in effluent toxicant concentrations occurred within the 50% TOC breakthrough zone, and within the 75% breakthrough zones of all three surrogate parameters. Again, ambiguity regarding when these points occurred diminishes the validity of this approach to column monitoring. This phenomenon is closely tied to the second major inadequacy of the surrogate parameter monitoring techniques examined in this study; insensitivity to individual toxicant breakthrough.

Figure 39 depicts percentage breakthrough curves for selected toxicants and surrogate parameters from the eleven-component wastewater matrix. It is apparent from this graph that neither TOC nor COD (digestion) parameters provided an accurate reflection of the breakthrough of low affinity toxicants. Early in the column run when TOC and COD breakthrough was rapid (indicating that column effluent was deteriorating) little leakage of spiked toxicants had occurred. However, within the time that 2-nitrophenol breakthrough increased from 20% to 80%, COD breakthrough increased less than 6% and TOC less than 11%. The insensitivity to changes in effluent toxicant level is undoubtedly largely a function of the rapid initial breakthrough displayed by surrogate monitoring parameters. Breakthrough of TOC and COD had reached 35-55% by the time significant levels of spiked toxicants had appeared in column effluents. At this point in the column run, TOC effluent levels were about 10 mg/l and COD levels approximately 60 mg/l. Thus, in subsequent column operation, breakthrough of spiked toxicants at the $\mu\text{g/l}$ level was masked by the high background level. The sensitivity of the monitoring parameters examined was insufficient to detect the relatively small contributions from breakthrough of spiked toxicants.

Results of these studies clearly indicate that effective carbon column monitoring must be based on detection of the most mobile (lowest affinity) toxicant of concern. The data suggest that column monitoring with TOC or COD parameters will be complicated by differences in the shape of the breakthrough curves for these parameters vs those observed for individual toxicants. The breakthrough pattern for surrogate monitoring parameters was characterized by rapid initial breakthrough, followed by a slow subsequent breakthrough rate. This breakthrough pattern resulted in poorly defined breakthrough points, and contributed to poor sensitivity in reflecting toxicant breakthrough. The data indicate that these phenomena will necessitate more specific monitoring techniques to achieve the sensitivity required for effective column monitoring. The data further suggest that even if a surrogate parameter of sufficient sensitivity is

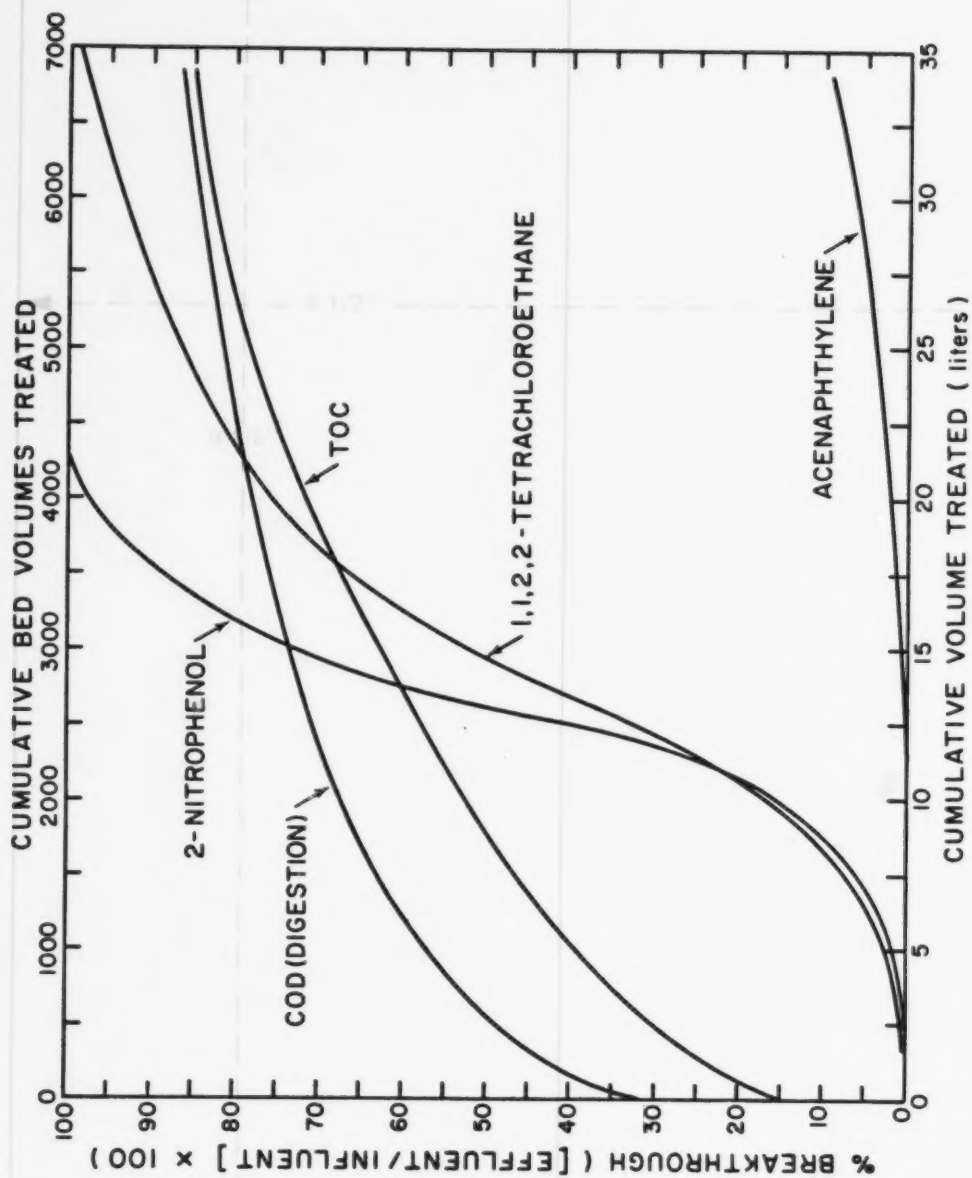


Figure 39, Toxicant breakthrough vs. breakthrough of surrogate parameters from eleven-component wastewater matrix.

employed, the breakthrough relationships between this parameter and individual toxicants must first be established. Even then, the complexity and variability of competitive adsorption interactions indicate that an extremely consistent column influent will be required to insure effective monitoring.

OTHER CONSIDERATIONS

Types of Active Carbon

The eleven component DIW matrix was used for comparison of the adsorptive properties of virgin Calgon Filtrasorb 400, regenerated Calgon Filtrasorb 400, and virgin Witco 950 activated carbons. Results of these studies (Figures 18-28) show that the virgin Calgon Filtrasorb 400 (F-400) carbon exhibited the highest adsorptive capacity for all eleven toxicants. However, adsorption patterns were quite similar for all three carbons, and capacity differences between the virgin F-400 and either of the other carbons were minimal for several of the spiked compounds. Up to the point at which these runs were terminated (approximately 9500 bed volumes treated), relative adsorbate-adsorbent affinities were identical for the virgin and regenerated F-400 carbons. A change in the position of 2,4-dimethylphenol and 1,4-dichlorobenzene was the only difference in relative carbon affinity noted for the Witco 950 adsorbent.

Inspection of these data (Figures 18-28) reveals that several distinct trends emerged in the comparative adsorption studies: 1) the adsorptive capacity of the regenerated F-400 carbon was greater than that of the virgin Witco 950 for all five phenolic species; 2) up to the point at which the runs were terminated, the adsorptive capacity of the virgin Witco 950 was greater than that of the regenerated F-400 for all other species (phthalates, PNA's, and chlorinated hydrocarbons); 3) the least difference in adsorptive capacity between any of the three carbons was observed for high affinity components; and, 4) the greatest difference in adsorptive capacity between the virgin F-400 and both other carbons was observed for the lowest affinity compounds (phenol and 1,1,2,2-tetrachloroethane). The latter two observations may be a function of the point at which these runs were terminated. It is quite possible that subsequent column operation would result in comparable capacity differences for high affinity compounds as these compounds approached complete breakthrough.

Although no attempt was made to thoroughly evaluate adsorbent characteristics, manufacturers literature provided no obvious reasons for the lower capacity the Witco carbon exhibited for phenolic adsorbates. Surface area, density, iodine number, and mean pore radius are comparable for both Witco 950 and Calgon F-400 carbons. However, differences in carbon surface functional groups provide a likely explanation for the adsorption variations observed. Since these carbon are produced from very diverse source materials (F-400 is coal based and Witco 950 is petroleum based) the activation process would, at very least, result in

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differing proportions of given surface functional groups. Because of the influence of competitive adsorption on removal of individual solutes, relatively slight changes in carbon surface characteristics could affect significant changes in adsorbate-adsorbent affinity in competitive adsorption environments.

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The very nearly comparable adsorptive capacity exhibited by the regenerated F-400 carbon is particularly encouraging in terms of treatment application. Removal capacity of the regenerated carbon proved to be almost equal to the virgin material, and superior to the Witco carbon, for several of the toxicants tested. Decreases in capacity for individual toxicants for the regenerated F-400 carbon ranged from 0.1-7.5% at the termination of the column runs. The decrease was less than 1.0% for six of the eleven compounds, and less than 2% for nine of the eleven. The greatest capacity decreases were observed for the two lowest affinity components; 4.3% for 1,1,2,2-tetrachloroethane and 7.5% for phenol. Although the regeneration history of the F-400 carbon used in this study was unknown, these data indicate that little loss in adsorptive efficiency resulted from reactivation. The results suggest that economic feasibility of carbon treatment will not be significantly threatened on the basis of post-regeneration carbon performance. This is an important consideration in practical applications, because carbon regeneration is mandatory for cost effective treatment. Substantial reductions in adsorptive capacity upon regeneration, coupled with carbon mass losses, might well preclude GAC as an economically feasible treatment technique.

Reproducibility

Although the limitations of using small scale carbon columns are well understood, replicate runs proved to be reproducible. This was true of both single- and multiple-component adsorption matrices. Replicate runs of the single-component phenol systems used to evaluate the influent concentration-carbon capacity relationship yielded narrow 95% confidence intervals. Average carbon capacity values + 95% confidence intervals for replicate runs of these adsorption systems were as follows:

3000 mg/l influent - $2.87 \text{ mM/gm} \pm 0.04 \text{ mM/g}$ for $n=4$;
405 mg/l influent - $2.23 \text{ mM/gm} \pm 0.11 \text{ mM/g}$ for $n=3$; and,
102 mg/l influent - $1.72 \text{ mM/gm} \pm 0.23 \text{ mM/g}$ for $n=2$.

Reproducibility was also examined in competitive adsorption environments by running duplicate studies of the eleven-component DIW and wastewater matrices. Simple direct comparison of experimental data in these matrices was not possible because duplicate runs lacked common x-axis (cumulative volume treated) values. However, inspection of the data in Tables 36 and 37 reveals that breakthrough characteristics from replicate runs were consistent in both matrices. Similarly, examination of the complete breakthrough data for these matrices (Tables A1-A11) indicates that effluent toxicant levels were comparable for replicate runs over the duration of the column studies. This indicates that the columns were

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functioning reproducibly; it is conceivable but less likely that the degree of short-circuiting could have been replicated in all these runs. Reproducibility thus provides further evidence that channeling did not adversely effect results of bench scale investigations.

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SITE STUDIES

Examination of carbon surface adsorbate concentrations at various levels within a carbon column provides another approach for evaluation of toxicant breakthrough. In fixed-bed adsorbers, solute molecules are removed most rapidly and effectively by the upper layers of fresh carbon during initial stages of operation (Weber, 1972). Initially the mass transfer zone, or primary adsorption zone, is concentrated near the top (influent) end of the column. As influent continues to flow into the column, the top layers of carbon become partially saturated with solute and less effective for further adsorption. As a result, the primary adsorption zone moves downward through the column to regions of fresher adsorbent. Continued column operation results in a wavelike movement of the primary adsorption zone at a rate which is generally much slower than the linear velocity of the water or wastewater being treated (Weber, 1972). As the primary adsorption zone moves downward, more and more solute escapes in the effluent until complete breakthrough occurs when the primary adsorption zone reaches the effluent end of the column.

It has been shown that in multiple-solute adsorption systems primary adsorption zones can be identified for individual solutes (Suffet, 1980). Because breakthrough occurs as a wavelike progression of the primary adsorption zone, a longitudinal profile of carbon surface coverage with bed depth should provide a means of approximating the extent of carbon exhaustion for a given solute and thus provide a means of comparing relative affinities of multiple solutes. In this context, a column less than completely exhausted for any given solute should show a profile in which there exists a maximum in surface coverage, the location of which in the column is dependent on the degree of column adsorption and the relative affinity of the compound. In a complex wastewater matrix, the summation of the mass of all components adsorbed should be highest at the influent end of the column, diminishing to a minimum near the effluent end. Individual component maxima should be distributed throughout.

Extraction and analysis of carbon samples from both site-study columns showed toxicant movement profiles generally consistent with the wavelike progression described by other investigators (see Figures 29 and 30). With a few exceptions, movement profiles of given toxicants were quite similar in both site studies. Although several anomalies were observed, movement profiles followed three basic patterns, in which either: A) the top section showed the greatest surface coverage, with coverage in subsequent sections progressing toward zero or near zero at the effluent end of the column; B) the top several sections showed the greatest, and approximately equal coverage, with subsequent sections progressing toward zero or near zero; or, C) maximum surface coverage occurred below the top section(s), with successive sections progressing toward zero or near zero

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coverage at the effluent end of the column (Figures 29 and 30).

The first movement profile (profile A) exemplifies a breakthrough pattern in which the uppermost section of the column is approaching saturation, but the primary adsorption zone has not yet moved to lower column increments. PNA's and polychlorinated phenols generally exhibited this type of profile (particularly apparent for acenaphthene and acenaphthylene) which indicates that carbon capacity for these compounds has not yet reached exhaustion. The second type of profile (profile B) exemplifies a breakthrough pattern in which the upper section(s) have reached exhaustion, and the primary adsorption zone has progressed to lower carbon sections. This profile is characteristic of lower affinity compounds; the depth to which the primary adsorption zone has progressed determined whether or not such compounds had appeared in column effluents. Solutes exhibiting this type of surface coverage profile included phenol and 2-nitrophenol (5-80 site study). Of the toxicants selected for this study, these two species were found to be the lowest affinity components in bench-scale investigations; surface coverage profiles from site studies seem to support this conclusion. The third carbon surface coverage profile (profile C) implies that desorption or ineffective competition with other solutes for sites had occurred in the upper section(s) of the column. For compounds exhibiting this type of profile, the primary adsorption zone has progressed down the column. Replacement of previously adsorbed solute or more active adsorption by other system components results in a lower surface coverage in the upper sections of the column. This pattern is particularly evident for 4,6-dinitro-o-cresol, dimethyl phthalate, di-n-butyl phthalate, and anthracene (5-80 site study) 2,4-dichlorophenol (4-81 site study) and, to a lesser extent, for 2-chlorophenol (5-80 site study). Also noteworthy is the length of column over which a substantial surface coverage was observed for phthalate species. This pattern indicates that the mass transfer zones for these solutes is relatively long, reinforcing similar conclusions derived from bench scale-studies. The fluctuations in surface coverage profiles, particularly evident for 2,4-dimethylphenol and 1,4-dichlorobenzene (5-80 site study) are obvious anomalies which remain to be adequately explained. The 1,4-dichlorobenzene, in particular, showed a very high affinity for the carbon in the spiked component-bench scale studies. Its early appearance in the effluent samples from the site-study column (verified by GC/MS) is puzzling, but is felt to be related to either its low influent concentration or to transport enhanced by association with mobile, non-adsorbing materials in the wastewater. Experimental error associated with the extraction and GLC analyses of very complex samples provides another possible explanation for such inconsistencies. However, the comparative approach applied to the processing and analysis of these samples was intended to minimize this error.

It bears mentioning that although theoretical detection limits for the various components were the same in all of the studies, improved GLC techniques and greater care in sample and data handling in the 4-81 site study may have improved practical detection limits for these samples. The very low influent levels of the compounds of interest in this study undoubtedly made the researchers alert to minute concentrations in the column effluents that may have gone unnoticed in the much higher concentration spiked component studies. Even so, it is doubtful that data trends

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as pronounced as those presented for this study would have been overlooked in earlier studies.

Results from analyses of toxicant movement within the carbon columns support results of effluent breakthrough analyses in both site studies. Analyses of column effluent fractions from the 5-80 site study indicated that initial breakthrough had not occurred for any of the study toxicants. Examination of the surface coverage profiles for this column (Figure 29) shows that no carbon surface coverage was measured in fraction #7, the bottom (effluent) section of the column, for all study toxicants except for 2,4-dichlorophenol and 1,4-dichlorobenzene. No detectable surface coverage in the bottom fraction(s) indicates that these solutes were still being removed efficiently in upper column sections, so appearance in the effluent would not be expected. Surface coverage of 2,4-dichlorophenol and 1,4-dichlorobenzene in fraction #7 was considerably less than that observed in upper sections, suggesting that although the adsorption zone of these solutes had reached the bottom of the column, removal efficiency was still sufficient to prevent effluent breakthrough.

Surface coverage profiles were also generally supportive of results from effluent toxicant analyses for the 4-81 site study. With the exception of acenaphthylene, phenanthrene and 2-chlorophenol, some degree of surface coverage was observed in the bottom section (fraction #6) of this column for all study toxicants which were detected in column effluents (Figures 30 and 31). In contrast acenaphthene and 2,4,6-trichlorophenol showed surface coverage in fraction #6, but were not detected in column effluents.

Effluent breakthrough data from the 4-81 site study was consistent with the breakthrough trends observed in the bench-scale studies. Initial breakthrough of phenol and the monosubstituted phenols, shown to be low affinity compounds in the bench studies, also occurred early in the site study. In the site-study system, rapid initial breakthrough was observed for two of the three phthalate ester species monitored, providing further evidence that similar results from bench-scale studies were not an artifact of system channeling. Relative to other study toxicants, initial breakthrough of acenaphthylene and 1,4-dichlorobenzene unexpectedly occurred earlier in the site study than in bench-scale investigations but was generally in agreement with data from the 5-80 site study. Possible mechanisms for this phenomena were discussed earlier. Other PNA's and polysubstituted phenols exhibited an initial elution order consistent with bench scale results.

Quantitatively, initial toxicant breakthrough points occurred earlier in the 4-81 site study than in either the bench studies or the 5-80 site study. By 250 bed volumes treated, trace concentrations of ten of the study toxicants had been detected in effluents from the 4-81 site study column (Figure 31). In contrast, at the point where the 5-80 site study column run was terminated (270 bed volumes treated) none of the study toxicants had been detected in column effluents. Since influent toxicant concentrations were comparable in both studies (Tables 30 and 32) changes in the bulk of the wastewater matrix are suspected. Some differences in the carbon columns could have occurred, but these were minimized by a thorough preparation protocol. Initial toxicant breakthrough occurred at approximately equivalent column run points for dimethyl phthalate,

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but over 28 times more rapidly for acenaphthylene in the 4-81 site study than in the bench-scale systems. Within these extremes, initial breakthrough of common toxicants averaged about 8 times more rapidly in the 4-81 site study than in the bench-scale systems (Tables 36, 38, and 43). This observation is particularly significant in view of the fact that influent toxicant concentration levels were substantially higher in the bench-scale matrices. It would seem that either transport of these compounds through the columns was facilitated by interactions of these compounds with an organic fraction of low sorption affinity, or that other unmonitored high affinity components were competing for available carbon sites.

The accelerated initial breakthrough of individual toxicants observed in the 4-81 site-study column supports the supposition that channeling was not a significant factor in defining the shapes of breakthrough curves observed in bench studies since site study column dimensions were adequate to assure no channeling occurred. These data also very dramatically illustrate the pronounced effect of concentration on adsorption phenomena. The apparently reduced removal capacity for study toxicants in the unspiked wastewater matrix likely results from the direct effect of concentration on carbon capacity as well as the effect of concentration on competitive adsorption interactions. As discussed previously, carbon capacity for individual solutes decreases as solution concentration decreases because of a weaker gradient driving film diffusion. In addition to the direct effect, relative concentration level exerts a significant influence on the nature and extent of competitive adsorption interactions. In the unspiked wastewater matrix, the greater concentration of other unmonitored wastewater constituents, relative to the toxicants monitored in this study, likely afforded these compounds a competitive advantage. As a result, background components were more successful competitors for available adsorption sites, particularly those components of equal or greater carbon affinity than study toxicants. In conjunction with conclusions drawn from bench scale studies, these data strongly support the need for on site adsorption studies to accurately assess both economic and technological feasibility of GAC treatment in wastewater applications.

ECONOMIC IMPLICATIONS

Because of the risks inherent to extrapolation from small- to large-scale operations and potential effects of channeling in small-scale columns, the intent here is to address economic issues of GAC treatment only in terms of approximate carbon requirements. Specifically, consideration is given only to how toxicant breakthrough results obtained from bench-scale studies relate to carbon requirements for a facility treating a wastewater matrix of comparable composition to that used in this study. In order to evaluate economic aspects of GAC treatment in wastewater applications, column effluent guidelines and/or ambient water quality criteria must first be established for each toxicant of concern. Since such guidelines or criteria are at this point lacking for the toxicants used in these investigations, 1, 10, and 25 $\mu\text{g/l}$ were selected as representative of acceptable effluent toxicant levels for approximating GAC requirements.

Carbon utilization rate provides a convenient means of calculating carbon requirements. This parameter is defined as the mass of carbon exhausted per unit volume treated to the exhaustion point, where the exhaustion point is defined by a specified column effluent concentration level. For a system treating a wastewater of composition comparable to the eleven-component spiked wastewater matrix used for this study, carbon utilization rates calculated for 1, 10 and 25 µg/l exhaustion points are presented in Table 43. These values account for competitive adsorption effects, as values for individual species were calculated from removal data obtained in a competitive adsorption environment.

TABLE 43. CARBON UTILIZATION RATES FOR ELEVEN-COMPONENT WASTEWATER MATRIX

Compound	Assumed Influent Level (mg/l)	Carbon Utilization Rate (g/m ³) ⁽¹⁾		
		1 µg/l	10 µg/l	25 µg/l
Phenol	0.470	520	112	--- ⁽²⁾
2-nitrophenol	0.695	716	343	263
2-chlorophenol	0.643	343	232	174
2,4-dimethylphenol	0.610	343	209	174
2,4-dichlorophenol	0.815	343	263	209
Dimethyl Phthalate	0.970	520	134	---
Diethyl Phthalate	1.110	1093	131	68
Di-n-butyl Phthalate	1.390	1093	118	---
Acenaphthylene	0.760	174	112	89
1,1,2,2-tetrachloroethane	0.839	1093	716	408
1,4-dichlorobenzene	0.735	209	163	118

(1) Carbon utilization rates for exhaustion points specified.

(2) Column effluent did not attain this breakthrough level within the run time used.

The carbon utilization rate can be combined with flow considerations to make rough estimations of the amount of carbon required to affect varying effluent quality levels. For the purposes of this discussion an average flow of 15 MGD is assumed, and calculations are based on a regeneration cycle of 30 days. With these assumptions, the volume of water to be treated between regeneration cycles would be roughly 1.70×10^6 m³ (450X10⁶ gallons). Based on the above assumptions, the mass of carbon required to achieve the various effluent quality levels are presented in Table 44. At approximately \$1.25/kg of active carbon, a substantial investment would be required in carbon alone. In addition to the initial carbon investment, a 30 day regeneration cycle, at 6-7% carbon loss per cycle, would result in complete carbon replacement every 14-16 months. However, provided that initial toxicant breakthrough is an accurate indicator of subsequent column

performance, the site-study data indicates that comparable carbon exhaustion points will occur even more rapidly in treatment of the unspiked wastewater matrix.

TABLE 44. CARBON REQUIREMENTS FOR A 15 MGD TREATMENT FACILITY⁽¹⁾

Compound	Assumed Influent Level (mg/l)	Mass of Carbon Required(10 ⁵ kg) ⁽²⁾		
		1 µg/l	10 µg/l	25 µg/l
Phenol	0.470	8.85	1.91	--- ⁽³⁾
2-nitrophenol	0.695	12.19	5.83	4.47
2-chlorophenol	0.643	5.83	3.94	2.97
2,4-dimethylphenol	0.610	5.83	3.56	2.97
2,4-dichlorophenol	0.815	5.83	4.47	3.56
Dimethyl Phthalate	0.970	8.85	2.28	---
Diethyl Phthalate	1.110	18.58	2.24	1.16
Di-n-butyl Phthalate	1.390	18.58	2.02	---
Acenaphthylene	0.760	2.97	1.91	1.51
1,1,2,2-tetrachloroethane	0.839	18.58	12.19	6.94
1,4-dichlorobenzene	0.735	3.56	2.77	2.02

- (1) Based on carbon utilization rates calculated for an influent of composition comparable to the eleven-component spiked wastewater matrix and a 30-day regeneration cycle.
- (2) Mass of carbon required to affect the indicated effluent quality level.
- (3) Values could not be calculated from available breakthrough data.

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APPENDIX

TABLE A1. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: PHENOL

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
0.80	ND	0.87	ND	0.81	ND	0.96	ND
+	+	+	+	+	+	+	+
19.45	ND	20.22	ND	2.55	ND	2.79	ND
20.47	0.4	21.23	0.5	3.57	2.0	3.84	1.5
21.42	0.4	22.13	0.9	4.64	3.7	4.90	2.6
22.32	1.3	23.17	1.4	5.34	2.5	5.83	3.7
23.40	1.3	24.17	3.7	6.25	2.9	6.78	5.1
24.33	3.4	24.93	3.4	7.24	6.0	7.60	4.2
25.10	5.1	26.02	4.3	8.21	5.3	8.62	2.0
26.09	8.7	26.89	13.4	9.11	2.3	9.54	3.7
27.04	12.6	27.89	16.9	10.04	1.4	10.47	4.1
27.96	16.1	28.88	15.6	11.02	1.2	11.44	2.7
28.96	12.9	29.82	17.9	11.81	2.6	12.26	2.5
29.86	19.2	30.76	26.9	12.77	2.4	13.07	2.6
30.82	27.3	31.65	42.3	13.73	3.4	13.93	1.9
31.62	59.2	32.43	56.8	14.79	5.2	14.88	3.4
32.63	54.6	33.48	65.2	15.84	2.2	15.91	6.7
33.63	67.9	34.41	70.8	16.82	2.1	16.86	4.1
34.61	73.3	35.33	62.4	17.69	5.0	17.82	9.6
35.25	66.8	35.98	64.2	18.70	10.5	18.51	8.7
36.26	75.8	36.63	73.6	19.64	4.7	19.52	5.7
37.23	82.1	37.00	81.4	20.52	3.7	20.46	4.7
38.00	94.6	37.79	94.2	21.51	2.1	21.41	4.6
38.72	90.8	38.51	108	22.42	2.0	22.48	5.1
39.49	98.4	39.51	120	23.31	10.6	23.53	3.7
40.36	118	40.56	137	24.16	7.0	24.60	2.9
41.28	135	41.56	139	25.14	6.5	25.54	7.8
42.25	143	42.56	161	26.11	8.5	26.49	5.7
43.17	159	43.44	171	27.00	5.5	27.43	6.3
44.00	184	44.50	193	28.00	5.0	28.37	7.2
45.04	180	45.45	189	28.95	5.9	29.26	4.1
46.09	213	46.46	246	29.89	6.9	30.16	5.6
47.08	242	47.55	271	30.91	6.5	31.20	4.4
48.17	256	48.46	246	31.90	7.1	32.24	5.8
49.14	274	49.45	310	32.71	7.1	33.16	5.9
50.16	327	50.40	332	33.60	2.7	34.25	6.3
51.16	311	51.43	305				
52.18	322	52.44	341				
53.24	360	53.43	398				
54.25	429	54.47	529				
55.25	552						

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TABLE A2. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: 2-CHLOROPHENOL

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
0.80	ND	0.87	ND	0.81	ND	0.96	ND
↓	↓	↓	↓	↓	↓	↓	↓
23.40	ND	24.17	ND	4.64	ND	3.84	ND
24.33	0.3	24.93	0.5	5.34	1.2	4.90	0.9
25.10	0.8	26.02	1.0	6.25	2.9	5.83	3.7
26.09	1.1	26.89	0.7	7.24	4.1	6.78	4.4
27.04	1.2	27.89	1.1	8.21	8.3	7.60	7.5
27.96	1.0	28.88	1.3	9.11	13.9	8.62	10.6
28.96	1.5	29.82	2.2	10.04	17.4	9.54	18.3
29.86	4.3	30.76	4.2	11.02	40.2	10.47	16.7
30.82	12.3	31.65	12.2	11.81	43.8	11.44	36.8
31.62	15.6	32.43	15.7	12.77	88.9	12.26	51.9
32.63	14.6	33.48	13.9	13.73	155	13.07	95.6
33.63	23.6	34.41	21.9	14.79	163	13.93	141
34.61	22.3	35.33	20.8	15.84	172	14.88	175
35.25	28.4	35.98	27.8	16.82	185	15.91	186
36.26	29.9	36.63	29.8	17.69	206	16.86	200
37.23	33.4	37.00	36.5	18.70	217	17.82	192
38.00	31.1	37.79	37.8	19.64	227	18.51	215
38.72	37.5	38.51	38.8	20.52	238	19.52	232
39.49	43.5	39.51	43.5	21.51	248	20.46	260
40.36	49.1	40.56	49.6	22.42	277	21.41	251
41.28	47.7	41.56	47.5	23.31	293	22.48	291
42.25	52.9	42.56	53.3	24.16	304	23.53	291
43.17	56.7	43.44	55.2	25.14	316	24.60	328
44.00	62.0	44.50	67.7	26.11	332	25.54	331
45.04	66.1	45.45	67.7	27.00	364	26.49	311
46.09	70.3	46.46	82.5	28.00	392	27.43	376
47.08	78.8	47.55	96.3	28.95	404	28.37	401
48.17	89.8	48.46	113	29.89	420	29.26	416
49.14	119	49.45	119	30.91	418	30.16	427
50.16	127	50.40	116	31.90	439	31.20	440
51.16	106	51.43	121	32.71	462	32.24	446
52.18	103	52.44	110	33.60	497	33.16	478
53.24	115	53.43	133			34.25	522
54.25	127	54.47	158				
55.25	151						

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TABLE A3. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: 2-NITROPHENOL

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
0.80	ND	0.87	ND	0.81	ND	0.96	ND
+		+		+			
22.32	ND	21.23	ND	2.55	ND	1.83	<0.9
23.40	0.8	22.13	0.8	3.57	1.1	2.79	1.7
24.33	0.8	23.13	0.9	4.64	2.1	3.84	3.3
25.10	0.9	24.17	1.2	5.34	7.7	4.90	8.8
26.09	1.6	26.02	2.3	6.25	12.5	5.83	16.5
27.98	2.3	26.89	1.8	7.24	14.6	6.78	20.6
28.96	1.8	27.89	2.2	8.21	21.9	7.60	23.5
29.86	2.8	28.88	3.4	9.11	60.8	8.62	51.8
30.82	3.8	29.82	3.9	10.04	91.9	9.54	97.7
31.62	5.1	30.76	5.0	11.02	130	10.47	138
32.63	4.4	31.65	6.0	11.81	163	11.44	184
33.63	15.0	32.43	7.0	12.77	210	12.26	248
34.61	29.8	33.48	18.5	13.73	382	13.07	365
35.25	52.1	34.41	13.7	14.79	433	13.93	451
36.26	63.0	35.33	55.5	15.84	513	14.88	527
37.23	71.6	36.63	65.9	16.82	529	15.91	548
38.00	79.0	37.00	76.7	17.69	560	16.86	573
38.72	73.7	37.79	81.3	18.70	563	17.82	531
39.49	98.8	38.51	90.0	19.64	598	18.51	581
40.36	103	39.51	96.3	20.52	633	19.52	602
41.28	104	40.56	110	21.51	698	20.46	611
42.25	104	41.56	131	22.42	764	21.41	706
43.17	130	42.56	122	23.31	731	22.48	742
44.00	123	43.44	119	24.16	843	23.53	756
45.04	132	44.50	149	25.14	806	24.60	821
46.09	136	45.45	135	26.11	864	25.54	856
47.08	163	46.46	160	27.00	974	26.49	881
48.17	223	47.55	216	28.00	1028	27.43	958
49.14	269	48.46	259	28.95	996	28.37	1010
50.16	254	49.45	274	29.89	1034	29.26	1066
51.16	290	50.40	286	30.91	1121	30.16	1043
52.18	300	51.43	292	31.90	1075	31.20	1091
53.24	324	52.44	313	32.71	1065	32.24	1071
54.25	344	53.43	351	33.60	980	33.16	1086
55.25	379	54.47	370			34.25	1011

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TABLE A4. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: 2,4-DIMETHYLPHENOL

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
0.80	ND	0.87	ND	0.81	ND	0.96	ND
+	+	+	+	+	+	+	+
30.82	ND	31.65	ND	4.64	ND	3.84	ND
31.62	1.0	32.43	0.9	5.34	0.5	4.90	<0.5
32.63	1.8	33.48	1.1	6.25	0.5	5.83	2.1
33.63	0.6	34.41	1.4	7.24	2.5	6.78	5.3
34.61	<0.4	35.33	0.7	8.21	7.4	7.60	6.3
35.25	<0.4	36.63	0.8	9.11	8.2	8.62	9.5
36.26	<0.4	37.00	1.1	10.04	1.4	9.54	12.6
37.23	<0.4	37.79	1.3	11.02	20.1	10.47	19.7
38.00	<0.4	38.51	5.6	11.81	19.7	11.44	25.3
38.72	8.3	39.51	9.2	12.77	22.6	12.26	36.8
39.49	8.6	40.56	10.4	13.73	72.7	13.07	51.5
40.36	9.3	41.56	8.6	14.79	121	13.97	83.4
41.56	7.9	42.56	8.4	15.84	107	14.88	116
42.25	9.1	43.44	6.1	16.82	113	15.91	126
43.17	1.6	44.50	7.3	17.69	130	16.86	134
44.00	0.8	45.45	4.7	18.70	143	17.82	141
45.04	8.7	46.46	9.6	19.64	172	18.51	159
46.09	12.1	47.55	10.2	20.52	199	19.52	180
47.08	9.3	48.46	11.0	21.51	153	20.46	162
48.17	12.1	49.45	7.3	22.51	178	21.41	184
49.14	14.0	50.40	12.6	23.42	181	22.48	181
50.16	5.6	51.43	10.9	24.41	213	23.53	196
51.16	6.7	52.44	6.2	25.14	232	24.60	206
52.18	5.3	53.43	14.1	26.11	258	25.54	248
53.24	3.4	54.47	16.8	27.00	241	26.49	265
54.25	11.7			28.00	266	27.43	302
55.25	13.7			28.95	272	28.37	277
				29.89	292	29.26	293
				30.91	288	30.16	288
				31.90	306	31.20	302
				32.71	312	32.24	312
				33.60	341	33.16	333
						34.25	373

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TABLE A5. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: 2,4-DICHLOROPHENOL

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
0.80	ND	0.87	ND	0.81	ND	0.96	ND
↓	↓	↓	↓	↓	↓	↓	↓
30.82	ND	30.76	ND	4.64	ND	4.90	ND
31.62	8.2	31.65	3.5	5.34	1.0	5.83	1.7
32.63	6.9	32.43	6.2	6.25	0.8	6.78	3.6
33.63	3.1	33.48	8.8	7.24	12.2	7.60	17.9
34.61	10.0	34.41	9.4	8.21	19.2	8.62	24.1
35.25	11.8	35.33	10.6	9.11	22.9	9.54	30.7
36.26	13.5	36.63	10.5	10.04	35.6	10.47	42.1
37.23	13.4	37.00	12.7	11.02	59.0	11.44	56.7
38.00	23.4	37.79	16.3	11.81	52.8	12.26	66.9
38.72	18.0	38.51	17.4	12.77	84.2	13.07	71.6
39.49	24.8	39.51	18.4	13.73	130	13.97	120
40.36	24.4	40.56	21.6	14.79	156	14.88	126
41.28	19.4	41.56	20.3	15.84	146	15.91	148
42.25	22.1	42.56	21.1	16.82	157	16.86	163
43.17	18.5	43.44	19.9	17.69	173	17.82	176
44.00	19.4	44.50	20.7	18.70	178	18.51	185
45.04	16.7	45.45	22.4	19.64	241	19.52	208
46.09	15.8	46.46	17.5	20.52	220	20.46	231
47.08	14.9	47.55	24.1	21.51	235	21.41	256
48.17	28.0	48.46	28.6	22.42	249	22.48	283
49.14	35.6	49.45	31.4	23.31	232	23.53	296
50.16	29.7	50.40	29.6	24.16	277	24.60	310
51.16	26.1	51.43	27.7	25.14	290	25.54	301
52.18	28.7	52.44	34.7	26.11	336	26.49	342
53.24	24.6	53.43	32.9	27.00	401	27.43	387
54.25	29.6	54.47	43.5	28.00	409	28.37	408
55.25	39.4			28.95	406	29.26	420
				29.89	427	30.16	452
				30.91	444	31.20	474
				31.90	412	32.24	441
				32.71	474	33.16	493
				33.60	502	34.25	542

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TABLE A6. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: DIMETHYL PHTHALATE

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
0.84	ND	0.87	ND	0.81	ND	0.96	ND
11.02	ND	11.17	ND	2.55	ND	1.83	ND
11.90	<0.3	12.09	0.3	3.57	0.5	2.79	<0.4
12.67	<0.3	13.00	0.8	4.64	1.6	3.84	1.1
13.31	0.8	13.74	0.4	5.34	2.5	4.90	2.3
14.30	<0.3	14.20	0.3	6.25	1.8	5.83	2.0
15.17	<0.3	14.74	0.4	7.24	7.9	6.78	5.6
16.16	0.6	15.56	0.6	8.21	8.8	7.60	6.7
17.13	0.5	16.31	0.5	9.11	7.2	8.62	7.3
17.53	0.4	17.24	0.7	10.04	8.7	9.54	8.5
18.43	<0.3	18.23	0.6	11.02	16.0	10.47	8.4
19.18	<0.3	19.18	0.7	11.81	14.7	11.44	7.9
20.47	<0.3	20.22	0.6	12.77	4.7	12.26	6.4
21.42	0.3	21.23	1.0	13.73	2.2	13.07	9.3
22.32	<0.3	22.13	0.5	14.79	6.6	13.93	9.1
23.40	<0.3	23.17	0.7	15.84	5.2	14.88	10.6
24.33	<0.3	24.17	0.6	16.82	8.3	15.91	8.7
25.10	<0.3	26.02	1.0	17.69	3.9	16.86	6.5
26.09	<0.3	26.89	0.4	18.70	3.2	17.82	7.3
27.04	0.3	27.89	0.7	19.64	4.3	18.51	8.4
27.96	0.4	28.88	0.9	20.52	6.0	19.52	14.6
28.96	0.4	29.82	1.1	21.51	10.1	20.46	10.4
29.86	0.7	30.76	0.8	22.42	14.4	21.41	6.1
30.82	8.4	31.65	7.6	23.31	3.9	22.48	5.3
31.62	20.8	32.43	18.4	24.16	12.4	23.53	5.0
32.63	24.5	33.48	20.7	25.14	3.8	24.60	6.7
33.63	20.9	34.41	22.3	26.11	14.0	25.54	7.8
34.61	57.5	35.33	45.8	27.00	14.0	26.49	9.4
35.25	58.0	36.63	54.2	28.00	9.6	27.43	8.7
36.26	66.6	37.00	59.7	28.95	7.7	28.37	7.6
37.23	71.0	37.79	51.3	29.89	14.0	29.26	9.5
38.00	82.7	38.51	61.7	30.91	12.6	30.16	9.6
38.72	58.0	39.51	54.5	31.90	5.2	31.20	11.3
39.49	63.2	40.56	50.3	32.71	9.7	32.24	11.6
40.36	41.7	41.56	47.3	33.60	13.4	33.16	10.5
41.28	40.7	42.56	44.5			34.25	11.9
42.25	42.7	43.44	51.7				
43.17	40.6	44.50	48.6				
44.00	36.2	45.45	47.9				
45.04	46.3	46.46	52.7				
46.09	46.5	47.55	58.4				

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TABLE A6 . (CONTINUED)

VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
47.08	54.4	48.46	58.6				
48.17	52.4	49.45	62.3				
49.14	59.5	50.40	59.4				
50.16	65.5	51.43	66.7				
51.16	55.2	52.44	68.3				
52.18	64.1	53.43	62.5				
53.24	59.1	54.47	76.7				
54.25	73.5						
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TABLE A7. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: DIETHYL PHTHALATE

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc. (PPB)	Cum. Vol. Treated(L)	Effluent Conc. (PPB)	Cum. Vol. Treated(L)	Effluent Conc. (PPB)	Cum. Vol. Treated(L)	Effluent Conc. (PPB)
0.84	ND	0.87	ND	0.81	ND	0.96	ND
11.02	ND	11.17	ND	1.70	<0.9	1.83	1.1
11.90	0.4	12.09	0.5	2.55	0.9	2.79	<0.9
12.67	0.5	13.00	1.1	3.57	1.3	3.84	<0.9
13.31	<0.4	13.74	0.4	4.64	2.7	4.90	1.6
14.30	<0.4	14.20	0.5	5.34	0.9	5.83	2.4
15.17	0.6	14.74	0.4	6.25	3.6	6.78	3.7
16.16	1.0	15.56	1.0	7.24	12.8	7.60	10.5
17.13	1.3	16.31	1.6	8.21	10.5	8.62	6.3
17.53	0.5	17.24	2.1	9.11	7.1	9.54	5.8
18.43	<0.4	18.23	0.8	10.04	16.5	10.47	<0.9
19.45	0.7	19.18	0.4	11.02	30.0	11.44	14.1
20.47	0.8	20.22	0.8	11.81	13.2	12.26	9.6
21.42	<0.4	21.23	1.3	12.77	21.0	13.07	16.7
22.32	<0.4	22.13	0.6	13.73	23.6	13.93	15.1
23.40	0.5	23.17	0.5	14.79	10.9	14.88	17.3
24.33	0.4	24.17	1.0	15.84	7.9	15.91	12.1
25.10	<0.4	26.02	0.5	16.82	9.9	16.86	8.6
26.09	0.4	26.89	0.4	17.69	6.4	17.82	7.3
27.04	0.6	27.89	0.6	18.70	7.3	18.51	9.5
27.96	0.4	28.88	0.7	19.64	34.6	19.52	12.3
28.96	1.1	29.82	0.9	20.52	4.8	20.46	6.7
29.86	7.9	30.76	1.4	21.51	3.1	21.41	5.6
30.82	18.7	31.65	5.7	22.42	3.8	22.48	8.3
31.62	17.3	32.43	12.8	23.31	9.9	23.53	5.9
32.63	20.6	33.48	19.4	24.16	8.3	24.60	6.7
33.63	11.7	34.41	20.7	25.14	10.1	25.54	10.5
34.61	24.7	35.33	22.6	26.11	4.4	26.49	11.6
35.25	21.1	36.63	33.4	27.00	15.3	27.43	11.9
36.26	22.5	37.00	24.1	28.00	17.1	28.37	12.3
37.23	40.2	37.79	41.1	28.95	40.3	29.26	28.7
38.00	71.0	38.51	48.5	29.89	38.9	30.16	14.6
38.72	44.1	39.51	55.6	30.91	13.5	31.20	36.9
39.49	50.6	40.56	52.1	31.90	43.8	32.24	7.2
40.36	54.1	41.56	49.7	32.71	10.0	33.16	50.3
41.28	50.2	42.56	48.5	33.60	11.8	34.25	22.5
42.25	56.1	43.44	54.4				
43.17	49.1	44.50	56.7				
44.00	58.7	45.45	58.9				
45.04	56.6	46.46	51.9				
46.09	55.7	47.55	66.3				

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TABLE A7. (CONTINUED)

VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
47.08	58.0	48.46	54.3				
48.17	52.9	49.45	59.6				
49.14	60.9	50.40	62.1				
50.16	57.6	51.43	68.7				
51.16	63.4	52.44	77.4				
52.18	67.7	53.43	71.9				
53.24	72.0	54.47	87.4				
54.25	81.4						
55.25	96.7						

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TABLE A8. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: DI-N-BUTYL PHTHALATE

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
0.84	ND	0.87	ND	0.81	ND	0.96	ND
10.17	ND	11.17	ND	1.70	1.0	1.83	2.1
11.02	0.8	12.09	0.9	2.55	1.0	2.79	0.8
11.90	1.9	13.00	1.4	3.57	2.1	3.84	2.7
12.67	1.7	13.74	1.2	4.64	2.2	4.90	3.5
13.31	2.5	14.20	1.9	5.34	1.3	5.83	1.7
14.30	1.2	14.74	1.2	6.25	2.0	6.78	2.4
15.17	1.2	15.56	3.4	7.24	2.6	7.60	3.1
16.16	0.8	16.31	4.0	8.21	0.6	8.62	2.6
17.13	3.4	17.24	4.3	9.11	1.5	9.54	2.9
17.53	3.7	18.23	2.9	10.04	9.1	10.47	7.8
18.43	1.2	19.18	0.9	11.02	5.1	11.44	1.7
19.45	0.8	20.22	2.2	11.81	1.4	12.26	2.4
20.47	2.7	21.23	2.4	12.77	4.4	13.07	5.9
21.42	3.9	22.13	2.0	13.73	4.8	13.93	6.3
22.32	1.7	23.17	1.6	14.79	2.7	14.88	4.9
23.40	1.8	24.17	1.3	15.84	3.2	15.91	3.1
24.33	2.3	26.02	1.9	16.82	2.9	16.86	15.7
25.10	2.6	26.89	2.0	17.69	2.0	17.82	5.8
26.09	2.6	27.89	2.5	18.70	5.8	18.51	6.4
27.04	2.0	28.88	2.2	19.64	2.9	19.52	3.1
27.96	2.5	29.82	3.1	20.52	2.8	20.46	9.3
28.96	2.0	30.76	12.7	21.51	4.1	21.41	14.6
29.86	4.4	31.65	22.4	22.42	3.5	22.48	3.7
30.82	16.7	32.43	28.7	23.31	7.3	23.53	1.1
31.62	36.9	33.48	33.1	24.16	5.1	24.60	4.3
32.63	34.8	34.41	22.1	25.14	3.8	25.54	2.0
33.63	15.3	35.33	25.2	26.11	2.0	26.49	1.9
34.61	18.2	36.63	27.3	27.00	2.1	27.43	3.6
35.25	14.4	37.00	48.9	28.00	3.0	28.37	2.7
36.26	30.9	37.79	59.2	28.95	2.8	29.26	4.8
37.23	55.6	38.51	67.3	29.89	13.9	30.16	5.9
38.00	90.4	39.51	60.8	30.91	9.1	31.20	6.3
38.72	60.1	40.56	75.4	31.90	10.9	32.24	4.1
39.49	80.1	41.56	81.7	32.71	11.6	33.16	3.7
40.36	79.2	42.56	73.2	33.60	12.9	34.25	5.4
41.28	63.1	43.44	75.4				
42.25	83.2	44.50	65.4				
43.17	66.9	45.45	63.2				
44.00	62.0	46.46	70.9				
45.04	75.0	47.55	70.8				
46.09	75.0	48.46	65.1				

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TABLE A 8. (CONTINUED)

VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
47.08	63.5	49.45	73.6				
48.17	65.7	50.40	78.5				
49.14	77.6	51.43	76.4				
50.16	75.2	52.44	80.7				
51.16	78.1	53.43	85.3				
52.18	76.9	54.47	99.7				
53.24	81.1						
54.25	96.4						
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TABLE A9. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: ACENAPHTHYLENE

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
0.80	ND	0.87	ND	0.81	ND	0.96	ND
+	+	+	+	+	+	+	+
29.86	ND	30.76	ND	10.04	ND	9.54	ND
30.82	0.7	31.65	1.0	11.02	1.5	10.47	0.9
31.62	2.6	32.43	1.7	11.81	2.5	11.44	2.8
32.63	1.3	33.48	2.1	12.77	3.2	12.26	3.6
33.63	0.6	34.41	1.4	13.73	3.0	13.07	4.6
34.61	1.0	35.33	1.9	14.79	3.5	13.93	5.1
35.25	1.6	36.63	2.6	15.84	5.0	14.88	3.4
36.26	3.5	37.00	4.8	16.82	4.6	15.91	7.9
37.23	6.6	37.79	4.7	17.69	5.5	16.86	9.8
38.00	4.6	38.51	5.6	18.70	19.8	17.82	12.5
38.72	5.4	39.51	8.3	19.64	18.1	18.51	14.7
39.49	7.2	40.56	10.1	20.52	19.2	19.52	19.8
40.36	11.5	41.56	10.9	21.51	19.0	20.46	20.6
41.28	12.9	42.56	9.8	22.42	20.0	21.41	16.4
42.25	13.8	43.44	12.1	23.31	22.3	22.48	25.1
43.17	10.0	44.50	10.5	24.16	19.1	23.53	28.3
44.00	9.7	45.45	11.7	25.14	25.8	24.60	31.1
45.04	12.5	46.46	13.1	26.11	54.5	25.54	22.6
46.09	11.4	47.55	12.4	27.00	41.8	26.49	41.7
47.08	9.0	48.46	12.1	28.00	43.0	27.43	48.9
48.17	9.3	49.45	13.9	28.95	51.0	28.37	50.6
49.14	11.8	50.40	14.1	29.89	53.0	29.26	55.7
50.16	12.3	51.43	12.7	30.91	43.9	30.16	57.9
51.16	13.5	52.44	17.7	31.90	64.1	31.20	55.6
52.18	9.9	53.43	14.8	32.71	57.2	32.24	58.3
53.24	13.0	54.47	15.6	33.60	59.2	33.16	60.4
54.25	13.6					34.25	62.7
55.25	15.1						

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TABLE A10. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: 1,4-DICHLOROBENZENE

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
0.80	ND	0.87	ND	0.81	ND	0.96	ND
+	+	+	+	+	+	+	+
27.96	ND	27.89	ND	9.11	ND	7.60	ND
28.96	3.8	28.88	2.0	10.04	0.9	8.62	0.8
29.86	2.7	29.82	3.2	11.02	0.9	9.54	1.7
30.82	3.2	30.76	3.1	11.81	1.8	10.47	2.4
31.62	4.7	31.65	4.6	12.77	4.7	11.44	3.8
32.63	5.6	32.43	5.4	13.73	9.8	12.26	15.2
33.63	6.3	33.48	5.2	14.79	12.6	13.07	12.3
34.61	10.6	34.41	16.2	15.84	14.5	13.93	14.9
35.25	12.2	35.33	12.4	16.82	16.4	14.88	17.2
36.26	16.4	36.63	15.7	17.69	26.4	15.91	19.5
37.23	18.8	37.00	22.2	18.70	37.8	16.86	24.8
38.00	18.2	37.89	20.3	19.64	30.4	17.82	29.7
38.72	14.8	38.51	16.0	20.52	31.6	18.51	32.6
39.49	14.0	39.51	14.0	21.51	36.8	19.52	34.7
40.36	17.2	40.56	15.9	22.42	31.8	20.46	37.9
41.28	17.6	41.56	17.2	23.31	43.7	21.41	31.5
42.25	15.7	42.56	15.5	24.16	31.8	22.48	41.2
43.17	15.9	43.44	17.0	25.14	52.5	23.53	46.8
44.00	21.3	44.50	20.8	26.11	66.8	24.60	48.9
45.04	20.4	45.45	19.7	27.00	61.3	25.54	55.9
46.09	17.4	46.46	24.5	28.00	66.6	26.49	67.6
47.08	21.6	47.55	20.7	28.95	49.1	27.43	71.4
48.17	19.2	48.46	33.1	29.89	71.1	28.37	69.8
49.14	25.7	49.45	29.6	30.91	56.8	29.26	64.3
50.16	28.4	50.40	33.8	31.90	68.9	30.16	67.7
51.16	35.8	51.43	30.8	32.71	67.5	31.20	72.4
52.18	29.2	52.44	26.1	33.60	81.9	32.24	74.6
53.24	21.2	53.43	27.5			33.16	79.9
54.25	25.9	54.47	31.1			34.25	90.8
55.25	37.0						

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TABLE A11. COMPARATIVE ADSORPTION FROM DUPLICATE ELEVEN-COMPONENT MATRICES: 1,1,2,2-TETRACHLOROETHANE

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VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
0.80	ND	0.87	ND	0.81	ND	0.96	<0.4
4.47	ND	4.66	ND	1.70	6.0	1.83	8.2
5.24	<0.8	5.55	0.8	2.55	7.5	2.79	12.1
6.31	0.9	6.23	0.9	3.57	13.2	3.84	18.3
7.20	1.1	7.21	1.1	4.64	16.0	4.90	27.9
8.25	1.4	8.21	0.9	5.34	23.8	5.83	35.6
9.16	2.3	9.23	1.4	6.25	30.5	6.78	51.9
10.17	3.0	9.85	1.0	7.24	62.1	7.60	78.4
11.02	3.5	10.49	2.7	8.21	89.9	8.62	101
12.67	5.7	11.17	3.9	9.11	136	9.54	126
13.31	7.1	12.09	5.6	10.04	166	10.47	154
14.30	8.3	13.00	5.8	11.02	231	11.44	186
15.17	9.5	13.74	8.4	11.81	196	12.26	201
16.16	10.6	14.20	7.9	12.77	319	13.07	284
17.53	12.4	14.74	10.4	13.73	467	13.93	397
18.43	13.1	15.56	10.9	14.79	503	14.88	448
19.45	13.4	16.31	12.8	15.84	513	15.91	492
20.47	18.2	17.24	14.7	16.82	549	16.86	527
21.42	13.5	18.23	15.8	17.69	579	17.82	563
22.32	14.8	19.18	15.3	18.70	599	18.51	596
23.40	16.0	20.22	19.6	19.64	627	19.52	635
24.33	17.9	21.23	18.9	20.52	656	20.46	640
25.10	20.4	22.13	20.4	21.51	632	21.41	661
26.09	24.0	23.17	17.8	22.42	670	22.48	696
27.96	23.7	24.17	18.9	23.31	646	23.53	681
28.96	32.4	24.93	22.3	24.16	691	24.60	673
29.86	37.8	26.02	26.7	25.14	664	25.54	700
30.82	40.3	26.89	25.4	26.11	739	26.49	713
31.62	52.6	27.89	19.4	27.00	701	27.43	735
32.63	62.5	28.88	29.8	28.00	726	28.37	759
33.63	67.8	29.82	34.1	28.95	722	29.26	741
34.61	83.4	30.76	43.7	29.89	736	30.16	776
35.25	80.9	31.65	55.4	30.91	717	31.20	771
36.26	97.1	32.43	67.3	31.90	776	32.24	789
37.23	129	33.48	60.8	32.71	794	33.16	806
38.00	158	34.41	77.5	33.60	834	34.25	846
38.72	167	35.33	88.6				
39.49	175	36.63	119				
40.36	181	37.00	141				
41.28	207	37.79	163				

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TABLE A11. (CONTINUED)

VIRGIN CALGON F-400: DIW MATRIX				VIRGIN CALGON F-400: WASTEWATER MATRIX			
RUN #1		RUN #2		RUN #1		RUN #2	
Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)	Cum. Vol. Treated(L)	Effluent Conc.(PPB)
42.25	223	39.51	178				
43.17	244	40.56	198				
44.00	262	41.56	211				
45.04	289	42.56	237				
46.06	317	43.44	253				
47.08	384	45.45	300				
48.17	402	46.46	332				
49.14	433	47.55	392				
50.16	480	49.45	457				
51.16	496	50.40	471				
52.18	484	51.43	512				
53.24	509	52.44	531				
54.25	530	53.43	516				
55.25	576	54.47	544				

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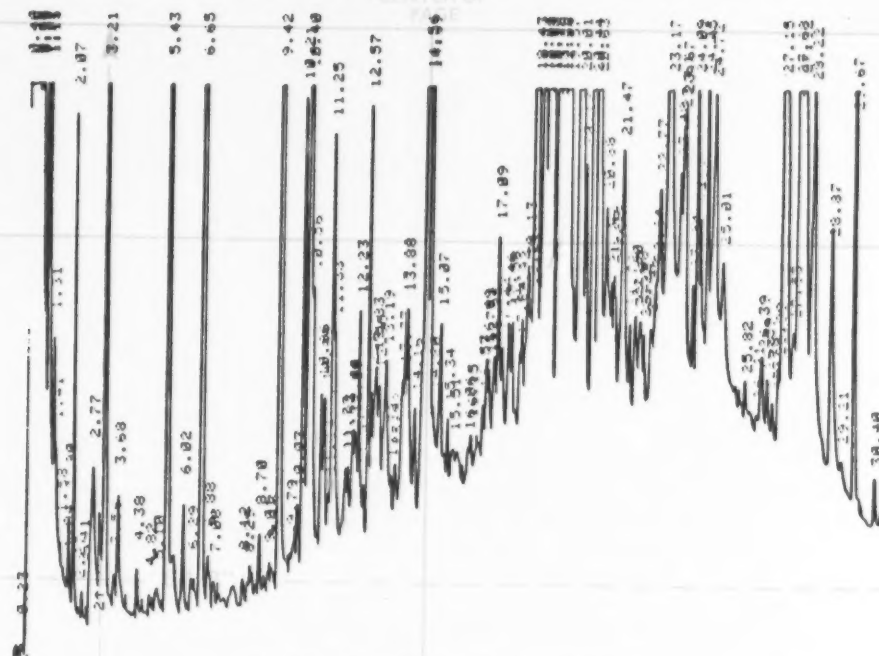
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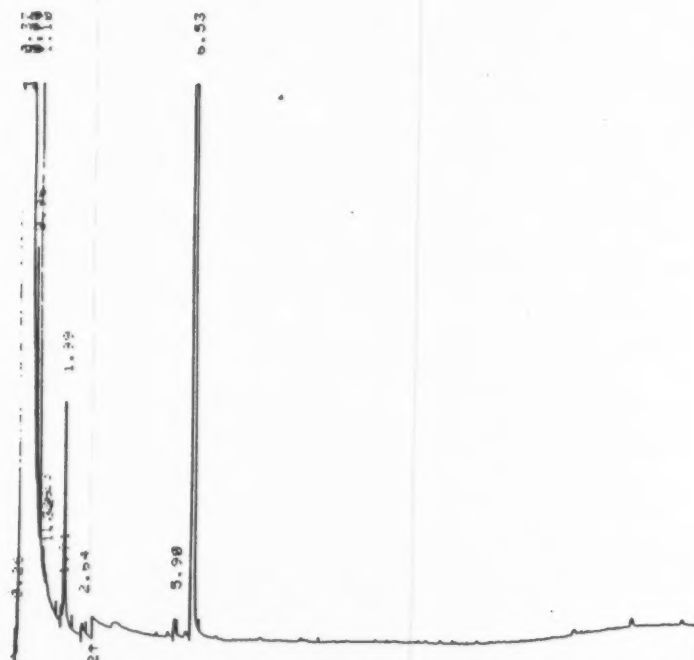
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A1-1) CARBON COLUMN INFLUENT



A1-2) COLUMN EFFLUENT FRACTION #1

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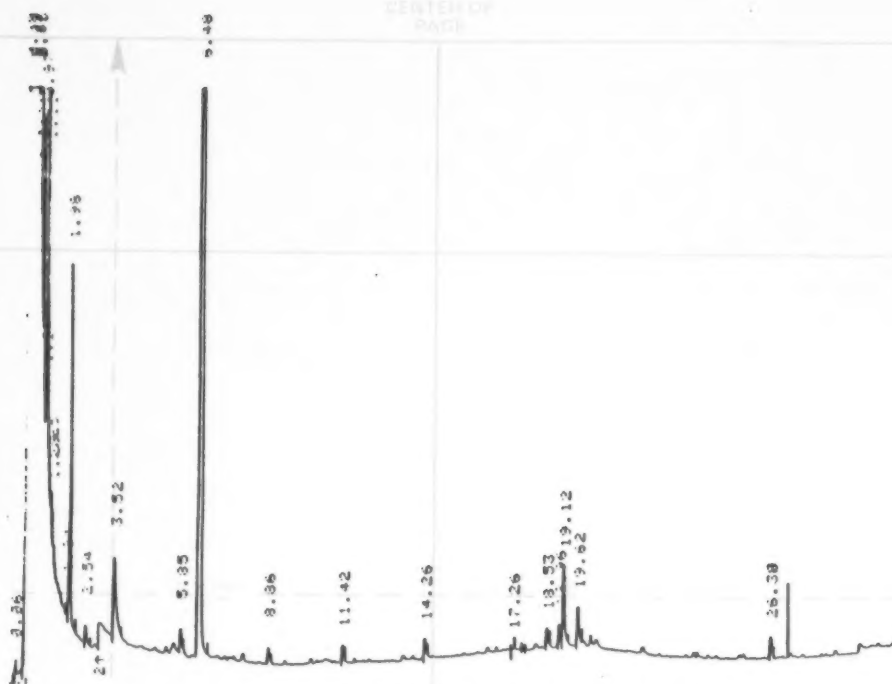
FIGURE A1. GAS CHROMATOGRAMS OF INFLUENT AND SELECTED EFFLUENT FRACTIONS
FROM THE ELEVEN-COMPONENT WASTEWATER MATRIX.

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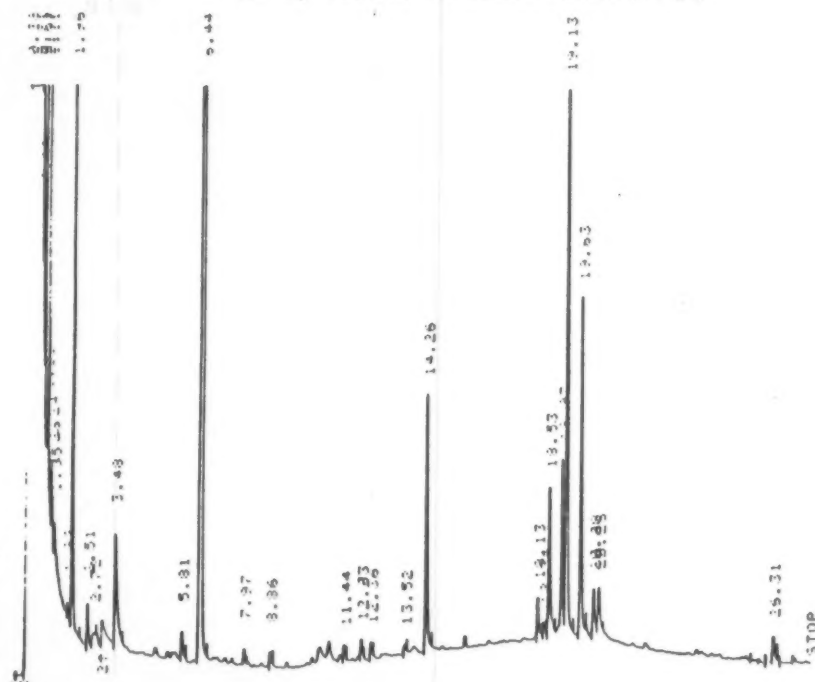
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A1-3) COLUMN EFFLUENT FRACTION #2



A1-4) COLUMN EFFLUENT FRACTION # 3

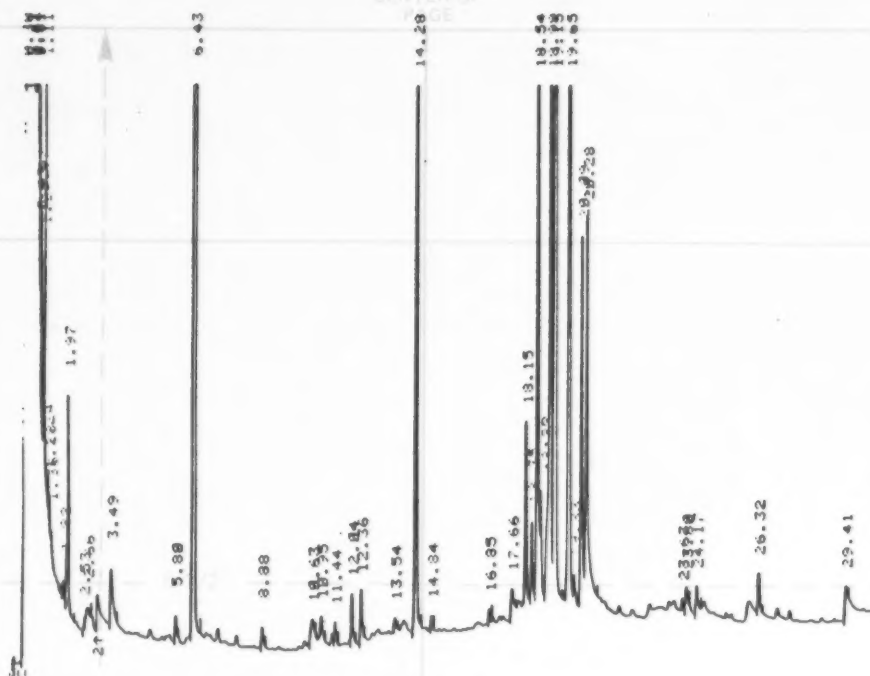
FIGURE A1 (CONTINUED)

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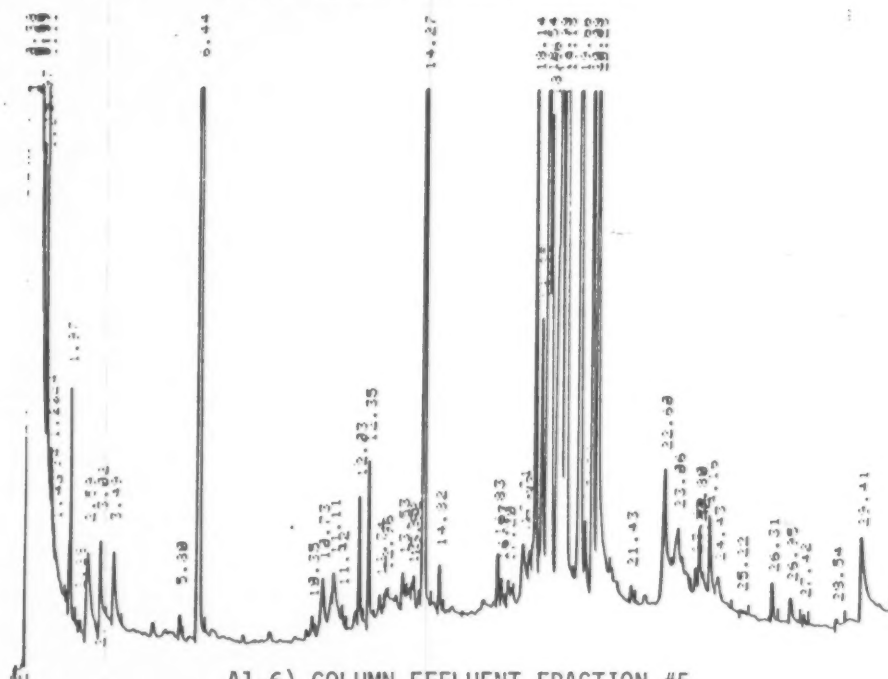
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A1-5) COLUMN EFFLUENT FRACTION #4

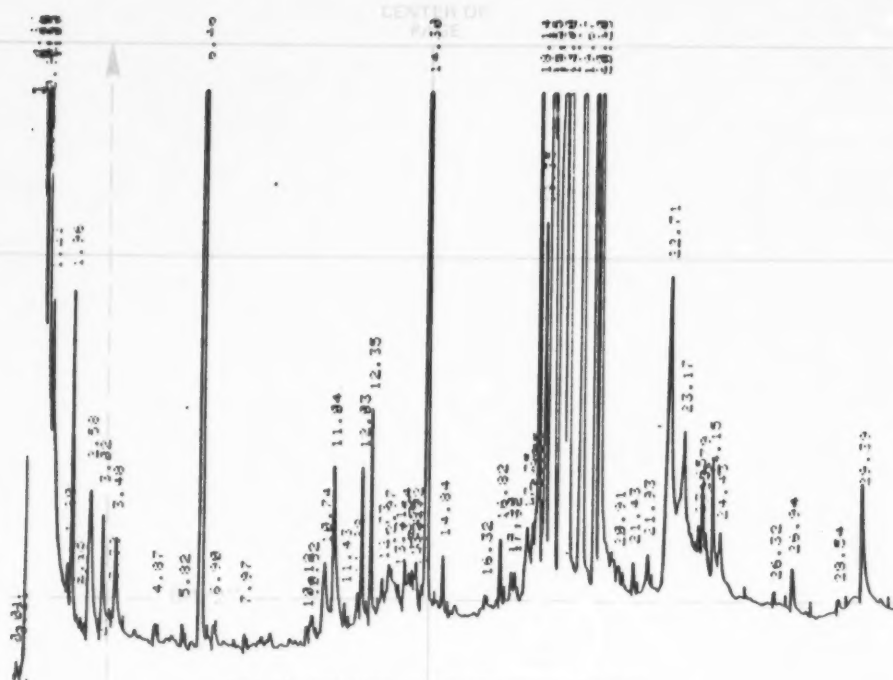


A1-6) COLUMN EFFLUENT FRACTION #5

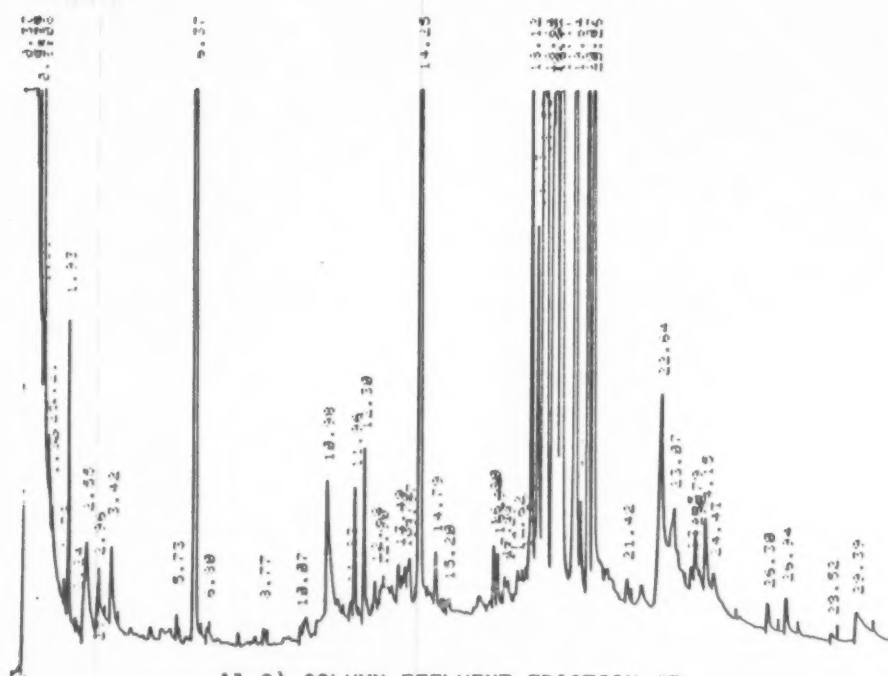
FIGURE A1 (CONTINUED)

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A1-7) COLUMN EFFLUENT FRACTION #6



A1-8) COLUMN EFFLUENT FRACTION #7

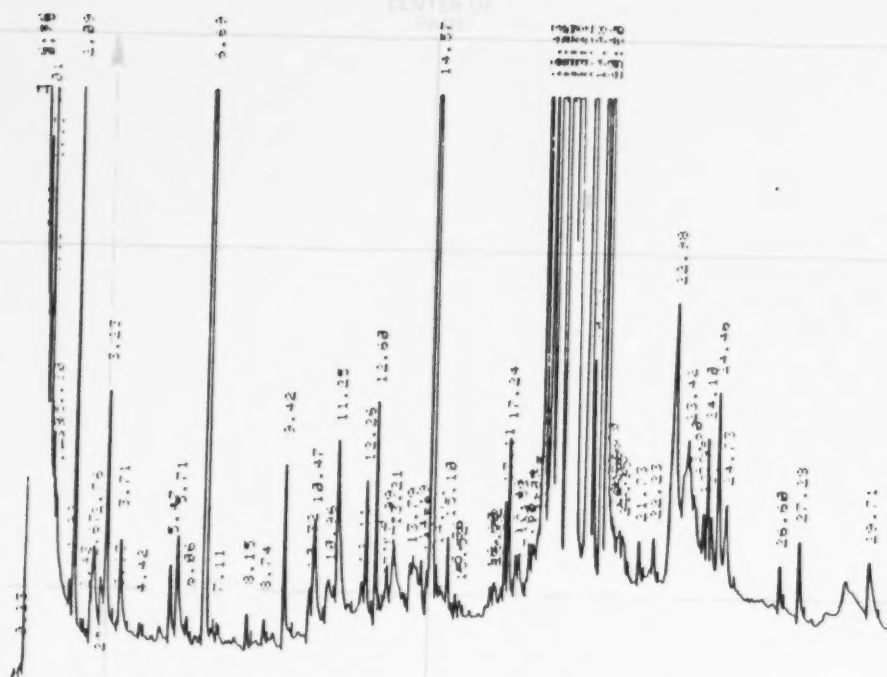
FIGURE A1 (CONTINUED)

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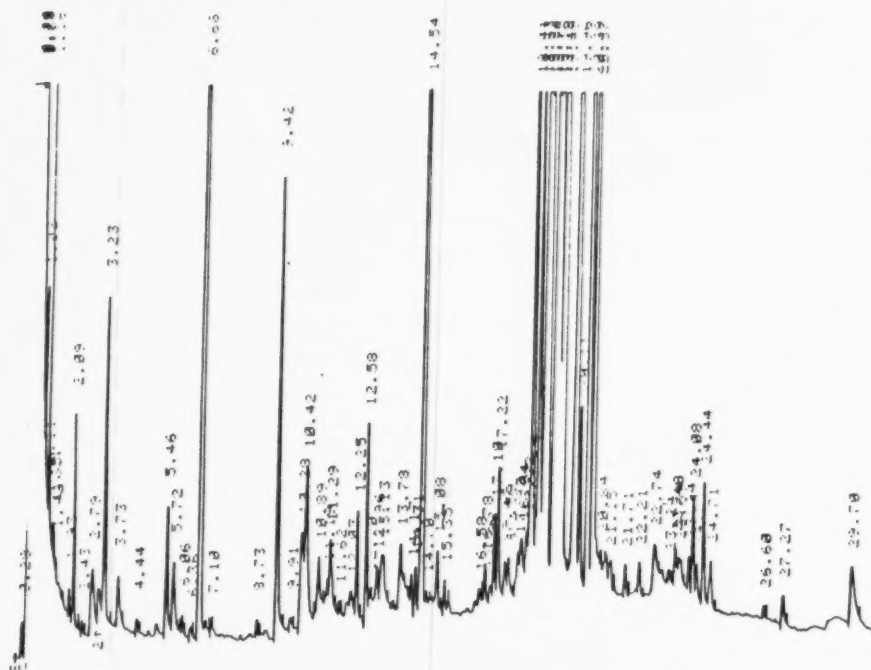
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A1-9) COLUMN EFFLUENT FRACTION #8

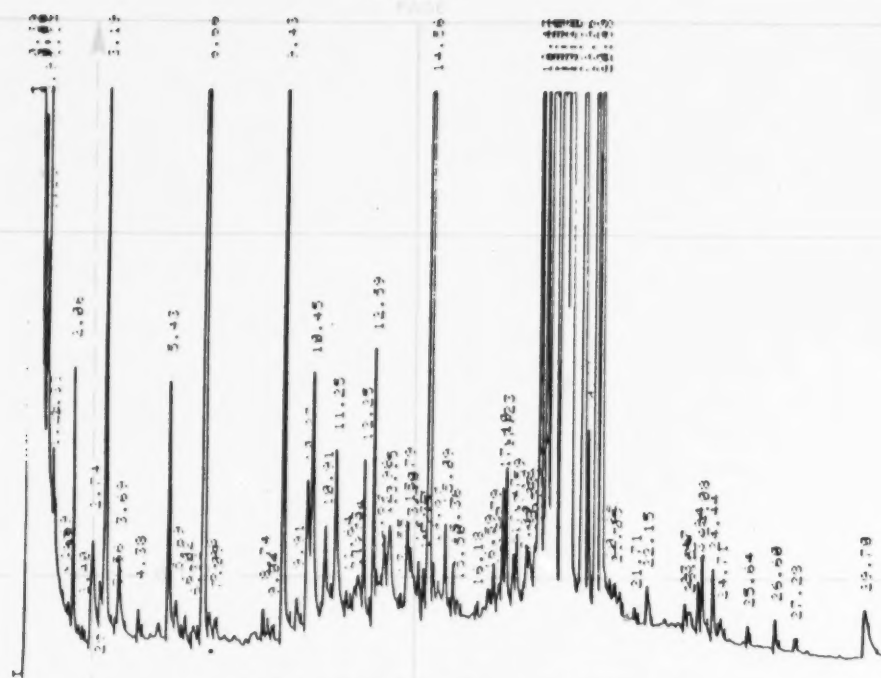


A1-10) COLUMN EFFLUENT FRACTION #9

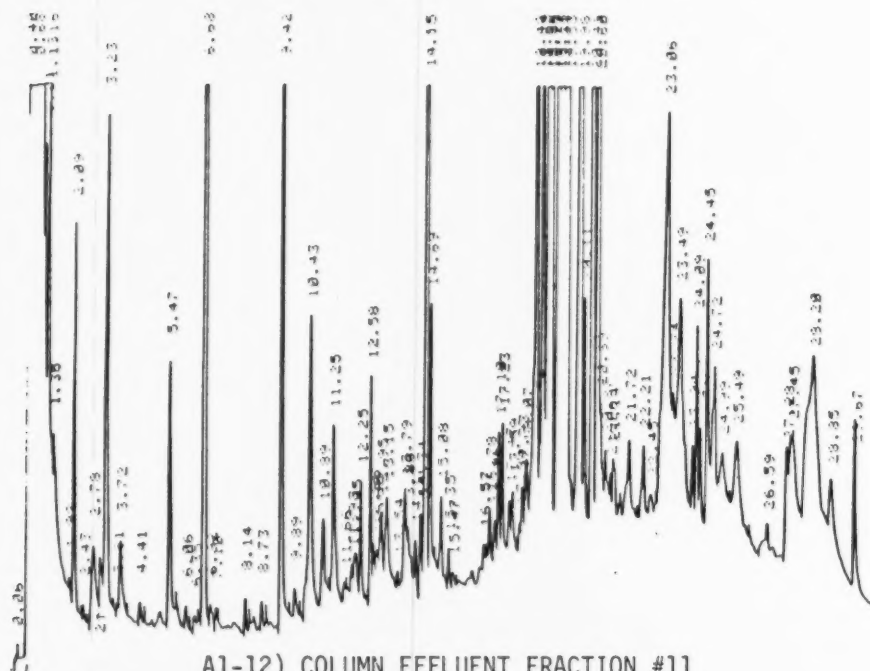
FIGURE A1 (CONTINUED)

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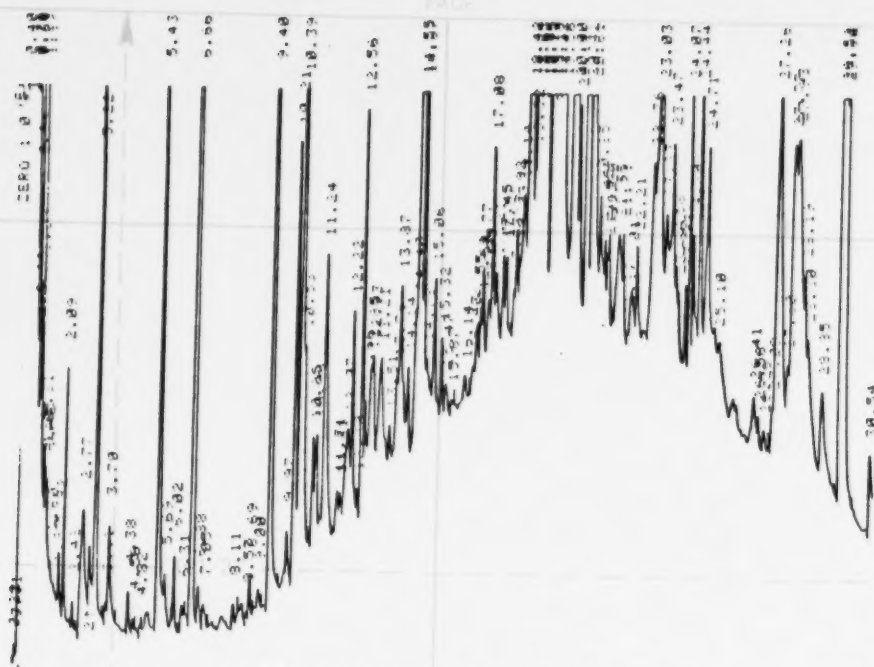


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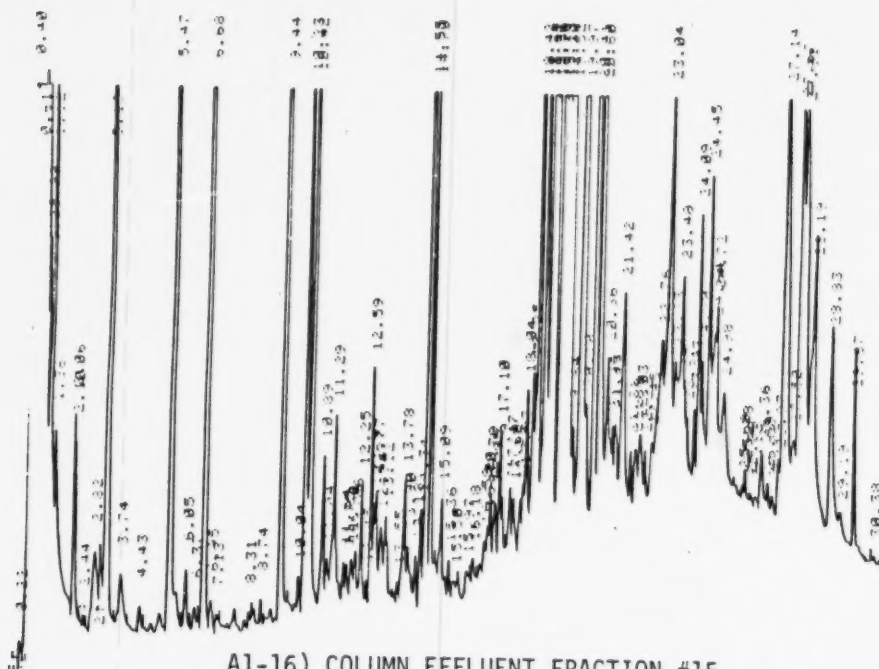
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A1-15) COLUMN EFFLUENT FRACTION #14



A1-16) COLUMN EFFLUENT FRACTION #15

FIGURE A1 (CONTINUED)

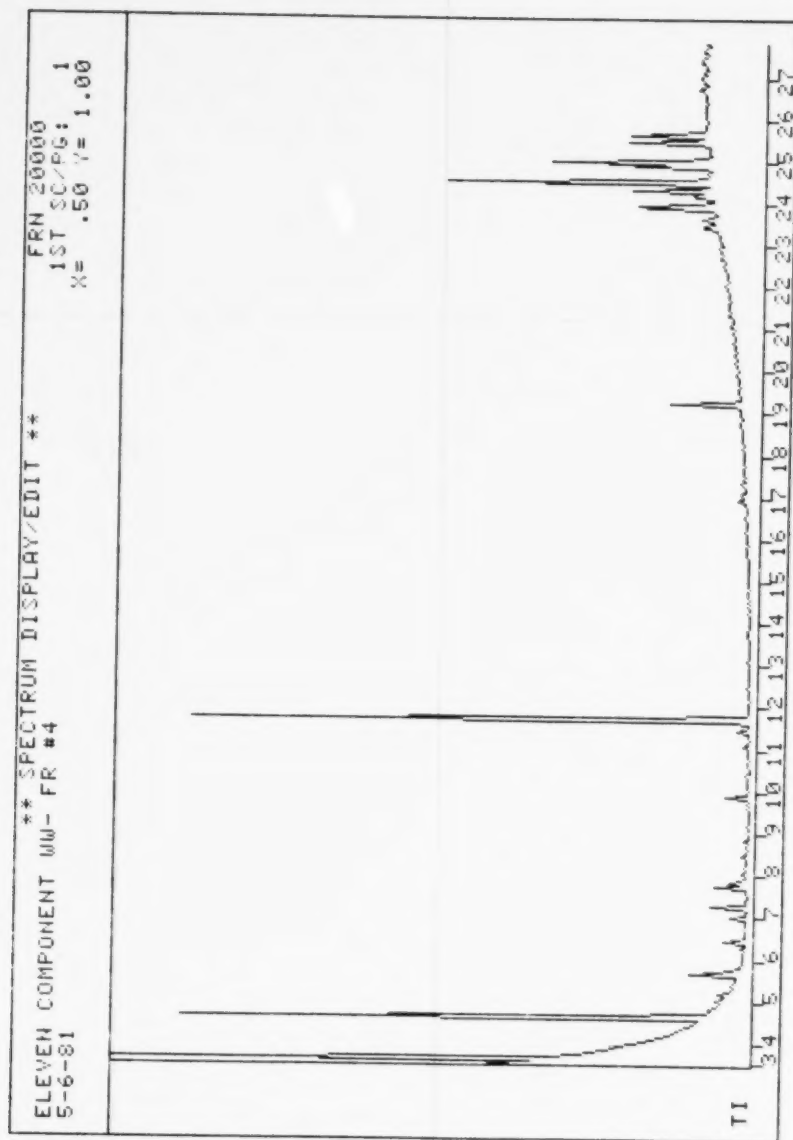


FIGURE A2. TOTAL ION CHROMATOGRAM OF COLUMN EFFLUENT FRACTION #4 FROM
 THE ELEVEN-COMPONENT WASTEWATER MATRIX.

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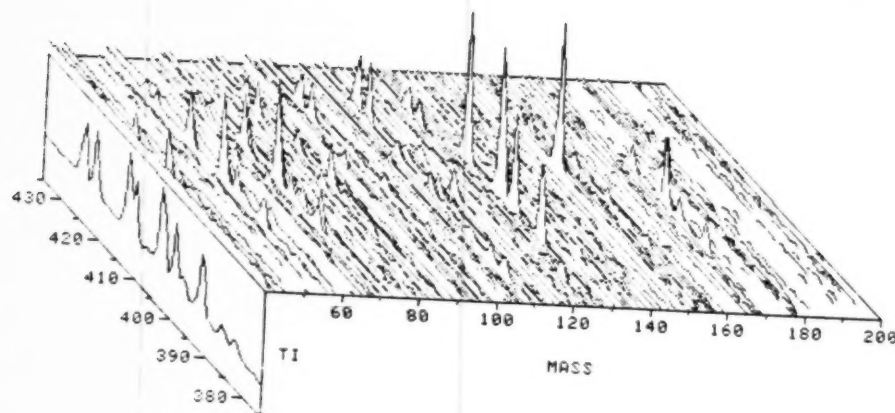
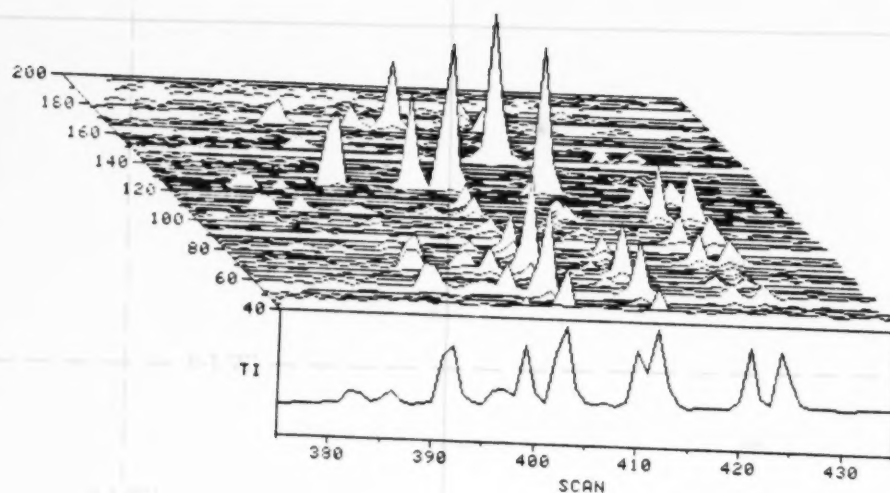


FIGURE A3. THREE-DIMENSIONAL PLOTS OF SCAN NUMBER VS MASS FOR COLUMN EFFLUENT FRACTION #4 FROM THE ELEVEN-COMPONENT WASTEWATER MATRIX.

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